BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A II—Organic Chemistry

JANUARY, 1944.

I.—ALIPHATIC.

Modern methods of preparative organic chemistry. V. Introduction of fluorine into organic compounds. W. Bockemüller. **VI. Use of biochemical oxidations and reductions for preparative purposes.** F. G. Fischer. **VII. Molecular distillation.** F. Wittka (*Angew. Chem.*, 1940, **53**, 419—424, 461—471, 557—568).—Reviews.

Isomerisation and alkylation of [saturated] hydrocarbons.—See B., 1943, II, 366.

Catalytic hydrogenation of carbon monoxide. Methane synthesis from water-gas.—See B., 1943, II, 365.

Alkylation of paraffins with olefines. Identification of the paraffins formed. A. V. Grosse and V. N. Ipatiev (*J. Org. Chem.*, 1943, **8**, 438—447; cf. A., 1935, 1348).—The hexanes formed by the catalytic alkylation of $CHMe_3$ with C_2H_4 in the presence of BF_3 or $AlCl_3$ are $CHMe_2Pr^{\beta}$ (90—70% of the total hexanes), $Pr^{\alpha}Pr^{\beta}$ (10—20%), and traces of $EtBu^{\gamma}$ (>3%). With both catalysts the relative amounts are approx. the same. Identification is accomplished by the isolation of $(CMe_2Br)_2$ and $NO_2{\cdot}CMe_2{\cdot}CEt(NO_2)_2$, m.p. 96°, and by their Raman spectra. The two other hexanes can be present only in negligible amounts if at all. Pr^{β}_2 probably arises by isomerisation of the primary $EtBu^{\gamma}$ but the origin of $Pr^{\alpha}Pr^{\beta}$ is obscure. H. W.

Kinetics of vinyl derivative polymerisation.—See A., 1944, I, 20.

End-group structure of polyvinyl alcohol. C. S. Marvel and G. E. Inskeep (*J. Amer. Chem. Soc.*, 1943, **65**, 1710—1714).—Hydrolysis (NaOMe) of polyvinyl acetate and re-esterification (C_5H_5N; Ac_2O; H_2SO_4–AcOH) of the alcohol (**I**) causes irregular increase or decrease in the degree of polymerisation. This is ascribed to the possible existence in (**I**) of a terminal CHO, which in acid can form acetals with the OH of other mols. of (**I**), whereas in alkali aldol or reverse aldol reactions can occur. R. S. C.

Geometrical isomerism of cyclic acetal derivatives from polyhydric nitro-alcohols.—See A., 1944, II, 23.

Preparation and purification of nitrated pentaerythritols.—See B., 1943, II, 367.

Isomeric $\alpha\gamma$- and $\beta\gamma$-benzylidene-*D*-arabitols. W. T. Haskins, R. M. Hann, and C. S. Hudson (*J. Amer. Chem. Soc.*, 1943, **65**, 1663—1667).—*D*-Arabitol (**I**) (1 mol.) and BzCl (2 mols.) in C_5H_5N at 0—5° and then room temp. give the *αε-dibenzoate* (**II**) (51%), m.p. 131—132°, $[\alpha]_D^{20}$ +8·4° in C_5H_5N, and thence the *αε-dibenzoate βγδ-triacetate*, m.p. 102—103°, $[\alpha]_D^{20}$ +31·0° in $CHCl_3$. The structure of (**II**) is proved by consumption of 1·94 and 2·02 mols. of $Pb(OAc)_4$ in AcOH in 30 and 60 min., respectively, with formation of 1 mol. of HCO_2H and 2 mols. of $OBz{\cdot}CH_2{\cdot}CHO$ (1·14 mols. isolated as cryst. semicarbazone). With PhCHO and $ZnCl_2$ at room temp. (**II**) gives *βγ-benzylidene*-D-*arabitol αε-dibenzoate* (**III**) (73%), m.p. 108—109°, $[\alpha]_D$ +12·6° in $CHCl_3$, and thence the *αε-dibenzoate δ-acetate*, m.p. 73—75°, $[\alpha]_D^{20}$ +2·1° in $CHCl_3$, and *αδε-tribenzoate* (**IV**), m.p. 101—103°, $[\alpha]_D^{20}$ −14·6° in $CHCl_3$. NaOMe–MeOH–$CHCl_3$ converts (**III**) into *βγ-benzylidene*-D-*arabitol* (90%), m.p. 81—83°, $[\alpha]_D^{20}$ +10·8° in EtOH, +18·1° in C_5H_5N, the structure of which (and of its forerunners) is proved by consumption of 1·05 mol. of aq. $NaIO_4$ with formation of CH_2O (0·74 mol. isolated as dimethone derivative) and syrupy 2 : 3-benzylidene-*D*-threose, the structure of which is proved by conversion into 2 : 3-*iso*propylidene-*D*-threose and thence *L*-tartaric acid and by hydrogenation (Raney Ni; EtOH; 25°/110 atm.) to syrupy *βγ*-benzylidene-*D*-threitol and thence *D*-threitol, m.p. 88—89°, $[\alpha]_D^0$ +4·6° in H_2O (dibenzylidene derivative, $[\alpha]_D^0$ −90·2° in C_5H_5N). Passing HCl into (**I**) and PhCHO at room temp. gives *αγ*-dibenzylidene-*D*-arabitol (**V**) (84%; conc. HCl gives only 10—11%), m.p. 151—152°, $[\alpha]_D^{20}$ −7·6° in C_5H_5N (cf. Fischer, A., 1894, i, 395), converted by BzCl–C_5H_5N into the *βδε-tribenzoate*, m.p. 137—138°, $[\alpha]_D'$ −133·8° in $CHCl_3$, which with H_2SO_4–Ac_2O–AcOH gives D-*arabitol βδε-tribenzoate αγ-diacetate*, m.p. 65—66°, $[\alpha]_D^{20}$ −8·2° in $CHCl_3$. H_2SO_4–Ac_2O–AcOH converts (**IV**) into D-*arabitol αδε-tribenzoate βγ-diacetate*, a syrup, $[\alpha]_D^0$ +19·1° in $CHCl_3$. The structure of (**V**) is thus proved (cf. Steifer *et al.*, A., 1934, 1364). M.p. are corr. R. S. C.

New form of crystalline xylitol. J. F. Carson, S. W. Waisbrot, and F. T. Jones (*J. Amer. Chem. Soc.*, 1943, **65**, 1777—1778).—Xylitol is obtained in a more stable *form*, m.p. 93—94·5°. Crystallo-optical data are given for this and the form of m.p. 61—61·5° (A., 1942, II, 389). R. S. C.

Two syntheses of polygalitol (αε-anhydro-*D*-sorbitol). N. K. Richtmyer, C. J. Carr, and C. S. Hudson (*J. Amer. Chem. Soc.*, 1943, **65**, 1477—1478).—Polygalitol (**I**) is a by-product in Zervas' synthesis of styracitol (A., 1930, 1160). Di-*β*-glucosyl disulphide octa-acetate with Raney Ni in EtOH gives slowly the tetra-acetate of (**I**), also obtained in poor yield similarly from *β*-glucothiose tetra-acetate, m.p. 74—75° (lit. 113—114°), $[\alpha]_D^{20}$ −8·3° → +47·0° in 12 weeks in 90% EtOH. R. S. C.

Aliphatic *β*-monoglycerides. B. F. Daubert, H. H. Fricke, and H. E. Longenecker (*J. Amer. Chem. Soc.*, 1943, **65**, 1718—1720).—*αγ*-Benzylideneglycerol with RCOCl in C_5H_5N at 20° gives *αγ-benzylideneglyceryl β-hexoate*, m.p. 34·1°, and *β-octoate*, m.p. 35·0°, converted by H_2–Pd-black–EtOH at 36 lb. into *glyceryl β-n-hexoate*, m.p. −8° to −10°, and *β-n-octoate*, m.p. 29·8°, respectively. R. S. C.

Series of αω-dimercaptans. W. P. Hall and E. E. Reid (*J. Amer. Chem. Soc.*, 1943, **65**, 1466—1468).—$[CH_2]_n(SH)_2$ (*A*) are prepared from the dibromides by $CS(NH_2)_2$ and then KOH in boiling H_2O in 80—85% yield; H_2S–NaOEt–EtOH–Et_2O at the b.p. gives 70—85% yields if $n > 6$, but if $n = 4$ or 5 yields are low owing to cyclisation. (*A*) of low mol. wt. are difficult to isolate because they are sol. in H_2O and tend to polymerise and to form $S([CH_2]_n{\cdot}SH)_2$. $CH_2(SH)_2$ could not be prepared. $[CH_2]_3(SH)_2$, m.p. −79°, b.p. 104·6°/100 mm., 172·9°/760 mm., is obtained in 40—50% yield by K xanthate + KOBz or by NHPh·CS_2M (M = Na or NH_4). The following are described: (*A*) in which $n = 2$, m.p. −41·2°, b.p. 146°, 4, m.p. −53·9°, b.p. 74·5°/10 mm., 195·6°/760 mm., 5, m.p. −72·5°, b.p. 90·1°/10 mm., 217·3°/760 mm., and 6, m.p. −21°, b.p. 106°/10 mm., 237·1°/760 mm.; *αη-dithiol*-n-*heptane*, m.p. −38·1°, b.p. 119·5°/10 mm., 252·2°/760 mm.; *αθ-dithiol*-n-*octane*, m.p. 0·9°, b.p. 132°/10 mm., 269·3°/760 mm.; *αι*-dithiol-*n*-nonane, m.p. −17·5°, b.p. 145°/10 mm., 284°/760 mm.; *ακ-dithiol*-n-*decane*, m.p. 17·8°, b.p. 161°/10 mm., 297·1°/760 mm.; *αλ*-dithiol-*n*-undecane, m.p. −5·4°, b.p. 171·5/10 mm., 308·8°/760 mm.; *αμ-dithiol*-n-*dodecane*, m.p. 28·4°, b.p. 181·5°/10 mm., 319·3°/760 mm.; *αα*-dithiol-*n*-octadecane, m.p. 52°; $[CH_2]_5(OH)_2$, m.p. −18°; $Br{\cdot}[CH_2]_n{\cdot}Br$ in which $n = 6$, m.p. −2·3°, 7, m.p. −41·7°, 9, m.p. −22·5°, and 11, m.p. −10·6°. *d*, *n*, and latent heats of evaporation are also recorded and regularities are noted. Suberic and azelaic acids are prepared by oxidising ricinoleic acid by $HNO_3 + NH_4$ vanadate (trace), removing the monobasic acids in steam, esterifying the dibasic acids, and fractionating the esters. R. S. C.

Sulphonium compounds. III. Reaction of organic sulphides with organic sulphates. F. E. Ray and J. L. Farmer (*J. Org. Chem.*, 1943, **8**, 391—396; cf. A., 1938, II, 135).—It is shown that rearrangements can occur during the formation of sulphonium sulphates and the mechanism proposed (*loc. cit.*) for the formation of sulphonium halides has been extended to these compounds. Me_2SO_4 and Me_2S react vigorously at 0°, giving the extremely deliquescent trimethylsulphonium methosulphate, which could not be isolated pure; it is hydrolysed to the sulphate, which forms a clear solution in H_2O. Addition of $BiCl_3$ to this solution leads to *tristrimethylsulphonium chloride dibismuth chloride*, $3SMe_3Cl,2BiCl_3$, decomp. 245°, also obtained from SMe_3Cl and $BiCl_3$; with a smaller proportion of $BiCl_3$ the product is *trimethylsulphonium chloride bismuth chloride*, m.p. 121—123°. A solution of $(CH_2Ph)_2S$ and Me_2SO_4 (1 : 1) in C_6H_6 is heated for 14 hr. at 100°, then hydrolysed by H_2O and treated with $BiCl_3$ followed by HCl, thereby giving *tribenzyldimethylsulphonium chloride dibismuth chloride*, m.p. 140°, decomp. 145°, whereas $(CH_2Ph)_2S$ and Me_2SO_4 (2 : 1) in hot AcOH afford tribenzylsulphonium sulphate, m.p. 173°, also obtained from $(CH_2Ph)_2S$, MeOH, and conc. H_2SO_4 in hot AcOH. Me_2S, $CH_2Ph{\cdot}OH$, and H_2SO_4 in glacial AcOH at room temp. afford *dibenzyldimethylsulphonium chloride bismuth chloride*, m.p. 138°, no rearrangement having occurred. A modified method for the determination of Bi is given (see C., 1944, Part I). H. W.

Identification of organic acids by partition between ethyl ether and water. O. C. Dermer and V. H. Dermer (*J. Amer. Chem. Soc.*, 1943, **65**, 1653—1654).—Many org. acids may be identified by shaking

50 ml. of 0·1N. aq. solution with 50 ml. of Et_2O (saturated with H_2O) at 25·0±0·5° and titrating the acid in each layer. Partition coeffs. are recorded for 61 acids. R. S. C.

Methyldiallylcarbinyl acetate. W. G. Young, L. J. Andrews, and S. J. Cristol (*J. Amer. Chem. Soc.*, 1943, **65**, 1657).—Adding CH_2:CH·CH_2·MgCl in Et_2O to AcCl in Et_2O gives *methyldiallylcarbinyl acetate* [*β-allyl-Δ⁵-pentenyl β-acetate*], b.p. 126—129°/192 mm., which is difficult to hydrolyse. R. S. C.

Esters of normal aliphatic alcohols and acids. J. H. Hoback, D. O. Parsons, and J. F. Bartlett (*J. Amer. Chem. Soc.*, 1943, **65**, 1606—1607).—The following are prepared from ROH, R'CO_2H, and *p*-$C_6H_4Me·SO_3H$ in C_6H_6: Pr, m.p. −68·7°, b.p. 85·28°/20 mm., Bu, m.p. −64·3°, b.p. 99·21°/20 mm., amyl, m.p. −47·0°, b.p. 116·6°/20 mm., *nonyl*, m.p. −22·3°, b.p. 173·3°/20 mm., *undecyl*, m.p. −10·5°, b.p. 198·4°/20 mm., *dodecyl*, m.p. −4·6°, b.p. 221·3°/20 mm., *tridecyl*, m.p. 6·9°, *tetradecyl*, m.p. 2·0°, and *pentadecyl* n-*hexoate*, m.p. 16·3°; Pr, m.p. −63·5°, b.p. 98—100°/20 mm., Bu, m.p. −67·5°, b.p. 112—114°/20 mm., and amyl heptoate, m.p. −49·0°, b.p. 118—119°/20 mm.; Pr, m.p. −45·0°, b.p. 112—113°/20 mm., Bu, m.p. −43·0°, b.p. 121—122°/20 mm., and amyl *n*-octoate, m.p. −34·5°, b.p. 124—126°/20 mm.; *Pr*, m.p. −36·0°, b.p. 120—122°/20 mm., *Bu*, m.p. −38·0°, b.p. 122—124°/20 mm., and *amyl* n-*nonoate*, m.p. −27·0°, b.p. 120—132°/20 mm. Temp. are corr. R. S. C.

Macromolecular compounds. CCXLVII. Constitution of highly polymerised synthetic materials. H. Staudinger and H. Warth (*J. pr. Chem.*, 1940, [ii], **155**, 261—298).—Interconversions of polyvinyl acetates (**I**) and alcohols (**II**) establish the macromol. nature of these compounds. A series of fractions of (**I**) are obtained from CH_2:CH·OAc polymerised in the cold and in absence of a catalyst; these are hydrolysed by NaOH–EtOH in dioxan in complete absence of air to (**II**), which are reacetylated by Ac_2O–C_5H_5N. Mol. wts. of (**I**) and (**II**) are determined osmometrically in H_2O and $\eta_{sp.}/c$ is observed for (**I**) in $COMe_2$ at 20° and (**II**) in H_2O at 20°. The K_m const. falls much below the calc. val. and is progressive. Oxidation of (**II**) with H_2O_2 lends no support to the hypothesis of the formation of branched chains during polymerisation since AcOH and CO_2 but no $(CH_2·CO_2H)_2$ could be detected. Closely similar observations are made with Me polyacrylate and polymethylacrylate. The viscosity law for linear colloids is valid for natural products such as cellulose and its derivatives and the mannans and for relatively simply polymerised synthetic materials; with more highly polymerised compounds divergencies occur as with the polyvinyl substances. Since in these cases the variations in K_m are continuous and there is no evidence that different branching is caused by differing conditions of polymerisation, it is probable that the mols. of polyvinyl compounds are not simply stretched in solution but are bent in a manner which is more pronounced as the complexity of the mol. increases. H. W.

Aluminium stearates. E. Eigenberger and A. Eigenberger-Bittner (*Kolloid-Z.*, 1940, **91**, 287—294).—Pptn. from alcoholic K stearate (acid or neutral) with aq. K alum (acidic, basic, or neutral) gives Al stearate of composition $(C_{18}H_{35}O_2)_{10}Al_8O_7,xH_2O$ (x = 8—12), which is const. on repptn. It is stable up to 110°, decomp. at 120°. All the stearic acid is replaced by alizarin (**I**) on boiling a PhMe + EtOH solution of Al stearate with (**I**), to give $(I)_{10}Al_8O_7$. Pseudo-Al stearates of higher Al contents are formed by addition of aq. alkaline K alum to neutral or acid K stearate, or of stearic acid to pptd. $Al(OH)_3$. These stearates show variable composition on repptn., and (**I**) is adsorbed as well as replacing stearic acid. The pseudo-salts are formed by peptisation of the $Al(OH)_3$ by stearic acid. J. H. Ba.

Preparation of acetoacetic esters of aliphatic alcohols.—See B., 1943, II, 367.

***p*-Nitro-, $[\alpha]_D^{20}$ −58°, and *p*-amino-benzyl ether, $[\alpha]_D$ −65°, −40°, of hyaluronic acid.**—See A., 1943, III, 925.

Activated oxalic acid.—See A., 1944, I, 21.

Conversion of maleic acid into maleic anhydride. Maleic anhydride purification.—See B., 1943, II, 367.

Preparation of nonane- and decane-αω-dicarboxylic acids. W. P. Hall and E. E. Reid (*J. Amer. Chem. Soc.*, 1943, **65**, 1468).—*μ*-Hydroxystearic acid is boiled with conc. HNO_3 + a little NH_4 vanadate; the monobasic acids are removed in steam, the dibasic acids are esterified, and the esters are fractionated and then hydrolysed. Thus is obtained ~40% each of $CO_2H·[CH_2]_n·CO_2H$ (n = 11 and 12). R. S. C.

Manufacture of unsaturated aldehydes.—See B., 1943, II, 368.

Oxygenation of crotonaldehyde. L. N. Owen (*J.C.S.*, 1943, 463—468).—CHMe:CH·CHO (**I**) in AcOH (equal vol.) containing known amounts of $Mn(OAc)_2$ is shaken in O_2 atm. at room temp.; the optimum amount of $Mn(OAc)_2$ is 2×10^{-6} mol. per l. The reaction products (except those from highest catalyst concns.) contain peroxides or per-acids. $Co(OAc)_2$ behaves similarly, but $Cu(OAc)_2$ has little effect. In absence of solvent Mn is detrimental at all concns., oxidation being most effective without any catalyst. Treatment of (**I**) with O_2 at 5 atm. resulted in an earlier separation of solid CHMe:CH·CO_2H (**II**), yield 70%. The highest yields of (**II**) are produced by oxygenating pure (**I**), avoiding undue rise of temp. From the steam-distillate of the reaction product a *bis*-2 : 4-*dinitrophenylhydrazone*, $C_{16}H_{14}O_8N_8$, m.p. 298°, is obtained, possibly a derivative of COEt·CHO. The part not volatile in steam yields cryst. *dl-erythro-αβ*-dihydroxybutyric acid. *Crotyl crotonate*, an oil, b.p. ~175°/770 mm., is synthesised by adding CHMe:CH·CH_2Br, b.p. 105—110°, to Ag crotonate in Et_2O. (**I**) gives a *compound*, $CaCl_2,2C_4H_6O$. H. Sch.

Aldol condensation. II. Reaction of *iso*butyraldehyde with its aldol. R. H. Saunders, M. J. Murray, and F. F. Cleveland (*J. Amer. Chem. Soc.*, 1943, **65**, 1714—1717; cf. A., 1943, II, 319).—When 10% KOH is added to $Pr^{\beta}CHO$–Et_2O containing a few drops of $NHBu_2$ at 5—10° and the product is washed with H_2O, distillation then gives <80% of the trimeride (**I**), b.p. 110—111°/8 mm., of $Pr^{\beta}CHO$; if the crude product is washed with 5% H_2SO_4, catalysis during distillation leads to formation of $Pr^{\beta}CHO$ and OH·CHPr^{β}·CMe_2·CHO (**II**). (**I**) and (**II**) are differentiated by Raman spectra, (**I**) having strong lines at 770, 798, and 1722, and (**II**) at 787 cm.$^{-1}$ The spectrum of the crude product shows complete absence of (**II**). The spectrum of (**I**) shows absence of CO. (**I**) is also obtained from (**II**) and $Pr^{\beta}CHO$ at room temp.; with boiling 15% KOH–EtOH it gives OH·CHPr^{β}·CMe_2·CH_2·OH and $Pr^{\beta}CO_2H$. (**I**) is the primary product of "aldolisation"; this accounts for the max. yield of (**II**) being 66·7%. It is probably 4-*hydroxy*-5 : *s*-*dimethyl*-2 : 6-*diiso*-*propyl*-1 : 3-*dioxan* and not $Pr^{\beta}CO_2$·CH_2·CMe_2·CHPr^{β}·OH as previously supposed. R. S. C.

Termolecular acetone peroxide in *iso*propyl ether. F. Acree, jun., and H. L. Haller (*J. Amer. Chem. Soc.*, 1943, **65**, 1652).—Distilling old Pr^{β}_2O in air gives, as residue, the trimeride, m.p. 98°, of acetone peroxide. R. S. C.

***βββ*-Trifluoro-ethylamine and -diazoethane.** H. Gilman and R. G. Jones (*J. Amer. Chem. Soc.*, 1943, **65**, 1458—1460).—$CF_3·CO·NH_2$ (prep. in 99% yield from $CF_3·CO_2Et$ by dry NH_3–Et_2O at 60—70°) with P_2O_5 at 145—150° gives $CF_3·CN$ (74%), b.p. −63·9°/743 mm., hydrogenated (PtO_2; Et_2O; 55—60°/1500 lb.) to *βββ*-trifluoroethylamine (**I**) (50—80%), b.p. 37—37·3°/737 mm. (**I**) is a very weak base; its *hydrochloride*, sublimes at >125°, reacts acid to Me-red. With aq. HNO_2–Et_2O, (**I**) yields *βββ-trifluorodiazoethane* (65—67%), yellow, which is stable in Et_2O for 6 weeks at room temp., is decomposed by acids, and with I–Et_2O gives slowly *αα-di-iodo-βββ-trifluoroethane*, m.p. −15° to −13·5°, b.p. 54°/39 mm. $CF_3·CH_2I$ is also prepared (no details). R. S. C.

Contiguously substituted aminodihydroxyalkanes. I. Syntheses of α-amino-βγ-dihydroxy-*n*-hexane and γ-amino-αβ-dihydroxy-*n*-hexane. C. Niemann, A. A. Benson, and J. F. Mead (*J. Org. Chem.*, 1943, **8**, 397—404).—Gradual addition of CH_2:CH·CHO to $MgPr^{\alpha}Br$ in Et_2O gives OH·CHPr^{α}·CH:CH_2, b.p. 90—94°/150 mm., converted by BzO_2H in $CHCl_3$ at 25° for 2 days into *αβ-expoxy-γ-hydroxy*-n-*hexane*, b.p. 87—90°/25 mm., which with conc. aq. NH_3 at 25° for 15 hr. affords *α-amino-βγ-dihydroxy*-n-*hexane* (**I**), b.p. 91°/0·06 mm., m.p. 53°. Oxidation of (**I**) by $NaIO_4$ or $Pb(OAc)_4$ follows the normal course but the yield of CH_2O is not even approx. quant. Equimol. amounts of (**I**), $CH_2Ph·O·COCl$, and NaOH yield *α-carbobenzyloxy-amino-βγ-dihydroxy*-n-*hexane* (**II**), m.p. 114—115°. (**I**) and Ac_2O in dry C_5H_5N at 25° afford *α-acetamido-βγ-diacetoxy*-n-*hexane*, m.p. 95·8—96·5°, hydrolysed by $Ba(OMe)_2$ in dry MeOH at 25° to *α-acetamido-βγ-dihydroxy*-n-*hexane* (**III**), b.p. 140—145°/0·11 mm. Oxidation of (**II**) or (**III**) requires 1 mol. of $NaIO_4$ or $Pb(OAc)_4$. The transformations OH·CHMe·CO_2Me → CHMeCl·CO_2Me → OMe·CHMe·CO_2Me → OMe·CHMe·CO$_2$H → OMe·CHMe·COCl are described in detail; the last substance could not be converted into OMe·CHMe·COPr$^{\alpha}$ (**IV**) by $ZnPr^{\alpha}I$. OMe·CHMe·CN, obtained from CHMeCl·OMe and dry CuCN, is transformed by $MgPr^{\alpha}Br$ into (**IV**), b.p. 92—93°/100 mm. (*semicarbazone*, m.p. 168·5—170°), reduced by HCO_2NH_4 and subsequently hydrolysed to γ-amino-β-methoxy-*n*-hexane, b.p. 95—98°/100 mm., which is converted by boiling HBr (*d* 1·5) into γ-amino-β-hydroxy-*n*-hexane, b.p. 95°/20 mm. (*di*-3 : 5-*dinitrobenzoyl* derivative, m.p. 207·2°). Passage of OEt·$[CH_2]_2$·OH vapour over Cu at 300—325° gives OEt·CH_2·CHO, b.p. 104—106°/747 mm., converted by HCl in abs. EtOH at 0° into OEt·CHCl·CH_2·OEt, b.p. 68·73°/30 mm. This is transformed by $Hg(CN)_2$ in boiling light petroleum (b.p. 60—70°) into *αβ-diethoxypropionitrile*, b.p. 96—98°/34 mm., which is converted by $MgPr^{\alpha}Br$ in dry Et_2O into *αβ-diethoxy*-n-*hexan-γ-one*, b.p. 114—116°/30 mm., hydrogenated at 150°/150 atm. in NH_3–MeOH containing Raney Ni to *γ-amino-αβ-diethoxy*-n-*hexane*, b.p. 85—87°/6 mm., 93—95°/10 mm., which is hydrolysed by HBr (*d* 1·5) to *γ-amino-αβ-dihydroxy*-n-*hexane* (**V**), b.p. 92—95°/0·1 mm.; the *carbobenzyloxy*-derivative, m.p. 109—110°, is oxidised in the usual manner by $NaIO_4$ or $Pb(OAc)_4$. It thus appears that the *N*-acyl derivatives of (**I**) and (**V**) have normal structures and that the stoicheiometry of the oxidation of these compounds by $NaIO_4$ and $Pb(OAc)_4$ is normal and predictable. Additional and substantial evidence in favour of the β-amino-αγ-di-

hydroxy-*n*-octadecane structure for dihydrosphingosine is thus provided although other structures are not definitely excluded. H. W.

Derivatives of *N*-carboxy-α-amino-acid esters. M. Frankel and E. Katchalski (*J. Amer. Chem. Soc.*, 1943, **65**, 1670—1674).—Passing CO_2 into $NH_2{\cdot}CHR{\cdot}CO_2R'$ in dry Et_2O at $<0°$ gives salts, $CO_2R'{\cdot}CHR{\cdot}NH{\cdot}CO_2NH_3{\cdot}CHR{\cdot}CO_2R'$ (cf. A., 1940, II, 7). Thus are prepared *salts* in which (*a*) R = H, R′ = Me (**I**) or Et (**II**), (*b*) R = Me, R′ = Et, (*c*) R = Ph, R′ = Et, and (*d*) R = Bu, R′ = Et. The salts are stable at 0° (dry) or in CO_2 at room temp., in air at room temp. absorb H_2O and evolve CO_2, dissolve unchanged in H_2O at 0° but with liberation of CO_2 at $<$ room temp., and in conc. acid liberate CO_2 quantitatively. Structures are proved as follows. With an aq. suspension of $Ca(OH)_2$, (**I**) gives Siegfried's salt, $\left.\begin{matrix}CH_2{\cdot}CO\\ NH{\cdot}CO\end{matrix}\right\rangle Ca$ (96%) (A., 1906, i, 324). CH_2N_2 in Et_2O at 0° converts (**II**) into $NH_2{\cdot}CH_2{\cdot}CO_2Et$ and $CO_2Me{\cdot}NH{\cdot}CH_2{\cdot}CO_2Et$, b.p. 127—129°/13 mm.; (**I**) gives similarly $NH_2{\cdot}CH_2{\cdot}CO_2Me$ and *N-carbomethoxyglycine Me* ester, b.p. 130°/20 mm., hydrolysed by conc. H_2SO_4 at room temp. to $CO_2Me{\cdot}NH{\cdot}CH_2{\cdot}CO_2H$, m.p. 95°. CH_2N_2–Et_2O similarly converts NH_4OBz into MeOBz and $EtCO_2NH_4$ into $EtCO_2Me$. R. S. C.

ε-*N*-Acetyl-lysine, m.p. 249—253° (decomp.), $[\alpha]_D$ +3·4±0·2°, and α-*N*-acetyl-*l*-lysine, m.p. 250° (decomp.), $[\alpha]_D$ +4·7°.—See A., 1943, III, 900.

Interaction of amides with amines. General method of acylation. A. Galat and (Miss) G. Elion (*J. Amer. Chem. Soc.*, 1943, **65**, 1566—1567).—The reaction, $NH_2R,HCl + R'CO{\cdot}NH_2 \rightarrow NH_4Cl + R'CO{\cdot}NHR$, is effected in 70—100% yield at 60°—the b.p. Examples are R = Me, Et, Pr, $CH_2{\cdot}CO_2H$, Ph, $C_6H_4{\cdot}OH$, tolyl, CH_2Ph, $Ph{\cdot}[CH_2]_2$, and $C_{10}H_7$ (also benzidine), and R′ = H, Me, Et, Pr$^\beta$, or Ph; $CO(NH_2)_2$ may be used at 250°. Hydrazines, but not guanidines, may be thus acylated. R. S. C.

Kinetics and mechanism of the racemisation of optically active cobalt trisdiguanide complex.—See A., 1944, I, 19.

Pilzcerebrin [cerebrin from lower plants]. II. F. Reindel, A. Weickmann, (Miss) S. Picard, K. Luber, and P. Turula (*Annalen*, 1940, **544**, 116—137).—Cerebrin (**I**), new formula, $C_{48}H_{93}O_5N$, m.p. 143—143·5°, is obtained pure only by way of its tetra-acetate, m.p. 67—68°, which is hydrolysed by KOH–MeOH at 50° (cf. A., 1930, 920). Anhydrocerebrin (**II**), $C_{48}H_{91}O_4N$, m.p. 116·5°, $[\alpha]_D$ +15·6° in C_5H_5N, best obtained from (**I**) (1 g.) by 0·06 g. of conc. H_2SO_4 in boiling MeOH (100 c.c.), is hydrolysed by conc. H_2SO_4 (3 g.) in boiling $Pr^\alpha OH$ (30 c.c.) to $C_{24}H_{48}{\cdot}CH(OH){\cdot}CO_2H$ (**III**), m.p. 103—105°, and a *base* (**IV**), $C_{20}H_{41}O_2N$, m.p. 87—89°, b.p. 245°/12 mm., $[\alpha]_D^{27}$ +31° in $CHCl_3$. (**IV**) is unaffected by H_2SO_4–MeOH and resists hydrogenation, but, when heated at 90°, in boiling C_6H_{14}, or rapidly in NH_3–EtOH, gives an *isomeride* (**V**), m.p. 100—101·5°, $[\alpha]^{27}$ +30° in $CHCl_3$. BzCl–C_5H_5N converts (**IV**) or (**V**) into the same *Bz*$_2$ derivative, m.p. 117·4—118°, hydrolysed by alcoholic alkali to a *Bz*$_1$ derivative, m.p. 105—106·5°, and thence ($Pr^\alpha OH$–$KOPr^\alpha$; with difficulty) to impure (**IV**). A mono-, m.p. 79—80°, and di-acetate, m.p. 69—71°, and picrolonate, m.p. 161—162°, of (**IV**) are also prepared. With $KMnO_4$–$COMe_2$, (**IV**) gives an *acid* (**VI**), $C_{15}H_{31}{\cdot}CO_2H$, m.p. 55·5—56° (*anilide*, m.p. 86·5—87°). Hydrolysis (HCl–MeOH; *loc. cit.*) of (**I**) gives (**III**), (**IV**), and a base (**VII**), now formulated as $C_{20}H_{43}O_3N$; a *product* (**VIII**), m.p. 108—109·5°, $[\alpha]_D$ +15·5° in $CHCl_3$ (cf. *loc. cit.*), is $C_{43}H_{90}O_6N_2$, formed by loss of H_2O from 2 mols. of (**VII**) and 1 mol. of $COMe_2$, and readily hydrolysed thereinto. With BzCl–C_5H_5N, (**VIII**) gives an oily product, converted by hot KOH–MeOH–H_2O into the *N-Bz* derivative, m.p. 130—131°, $[\alpha]_D^{18}$ +5·0° in C_5H_5N [with CrO_3–AcOH or $Pb(OAc)_4$ gives NH_2Bz], of (**VII**). $Pb(OAc)_4$ converts (**I**) in AcOH + a trace of Ac_2O into the *amide*, m.p. 122·5—124°, of (**III**), an aldehyde (**IX**), probably $C_{15}H_{31}{\cdot}CHO$, m.p. 28—32°, b.p. 155—165°/11 mm. [*polymer* (**X**), m.p. 63—64·5°; *semicarbazone*, m.p. 104—104·5°, hydrolysed by $C_6H_4(CO)_2O$ to (**X**); *thiosemicarbazone*, m.p. 81—83°; 2 : 4-*dinitro-*, m.p. 93·5—95° (corr.), and *p*-nitro-phenylhydrazone, m.p. 80—82°], and a substance (**XI**), $C_4H_8O_2$ [*di-p-nitro-*, m.p. 281—283° (decomp.), and *bis*-2 : 4-*dinitro-phenylosazone*, m.p. 295—297° (decomp.)]. (**XI**) is not formed directly by $Pb(OAc)_4$ in C_6H_6, but is obtained when the reaction products therefrom are heated in HCl–MeOH or 50% AcOH. (**III**) has $[\alpha]_D$ +2·1° in C_5H_5N, gives an acetate, m.p. 74—75°, and *anilide*, m.p. 88—89°, and with $Pb(OAc)_4$ in AcOH gives (?) HCO_2H and an aldehyde, m.p. 72—76° (*semicarbazone*, m.p. 115—115·5°; *p-nitrophenylhydrazone*, m.p. 104—105°), oxidised by CrO_3–AcOH to the acid, $C_{25}H_{50}O_2$, m.p. 81°, which is also obtained similarly from (**III**). M.p. show that (**III**), (**IX**), etc. contain a branched chain. For comparison, *n*-palmitaldehyde-2 : 4-dinitro-, m.p. 105—107° (corr.), margaraldehyde-*p*-nitro-, m.p. 96·5—97·5°, and -2 : 4-dinitro-phenylhydrazone, m.p. 103—105° (corr.), and -semicarbazone, m.p. 107—108·5°, are prepared. (**XI**) gives no colour with Schiff's reagent; its structure is uncertain but is not $OH{\cdot}CH_2{\cdot}CMe(OH){\cdot}CHO$ (no osazone) or $OH{\cdot}CHMe{\cdot}CH(OH){\cdot}CHO$ [di-*p*-nitrophenylosazone, m.p. 304° (decomp.)]. Acid hydrolysis of (**I**) leads to (**III**) + (**VII**) or, by way of (**II**), to (**III**) + (**IV**). Structures for (**I**) etc. are suggested. Ruppol's cerebrin, formulated as $C_{46}H_{91}O_4N$ (A., 1937, III, 484), is really (**I**). R. S. C.

Hydrogenation of aliphatic dinitriles. See B., 1943, II, 368.

Catalytic hydrogenation of adipodinitriles to produce hexamethylenediamines.—See B., 1943, II, 368.

Preparation of diazomethane. M. D. Owen (*Current Sci.*, 1943, **12**, 228).—$NH_2{\cdot}CO{\cdot}NMeAc$, m.p. 179—180°, obtained by slowly adding 10% NaOH to NH_2Ac and Br at 0° and then at 100°, is hydrolysed (boiling 3% HCl) and then converted by $NaNO_2$ into $NH_2{\cdot}CO{\cdot}NMe{\cdot}NO$, which can be kept in quantity at 0°. It is converted by aq. KOH in Et_2O into CH_2N_2. J. F. M.

II.—SUGARS AND GLUCOSIDES.

Chemical constitution and the tanning effect. II. Pentagallates of glucose and mannose. A. Russell, W. G. Tebbens, and W. F. Arey (*J. Amer. Chem. Soc.*, 1943, **65**, 1472—1474; cf. A., 1943, II, 61).—β-*d*-Glucose 1 : 2 : 3 : 4 : 6-pentagallate (**I**), softens 133°, sinters 143°, $[\alpha]_D^3$ +25·33° in EtOH, is obtained from the acetate by NaOH–NaOAc in aq. $COMe_2$–N_2. *d*-Mannose and 3 : 4 : 5 : 1-$(OAc)_3C_6H_2{\cdot}COCl$ in $CHCl_3$–quinoline at room temp. give d-*mannose penta*(*triacetylgallate*), sinters 121°, $[\alpha]_D^5$ −55·5° in $CHCl_3$, and thence, as above, d-*mannose pentagallate* (**II**), sinters 161°, $[\alpha]_D^{23}$ −72·38° in EtOAc. Similarly are obtained d-*glucose Et*$_2$ *mercaptal penta*(*triacetylgallate*), sinters 82°, $[\alpha]_D^{22}$ +18·75° in $CHCl_3$, and *pentagallate* (**III**), sinters 167°, $[\alpha]_D^{13}$ +11·13° in EtOAc, and thence (dil. H_2SO_4) aldehydo-d-*glucose pentagallate* (**IV**), sinters 113°, $[\alpha]_D^9$ +10·13° in EtOAc. (**I**)—(**IV**) make as good leather as does gallotannin. R. S. C.

Azoyl derivatives of sugars. [Their] separation by chromatographic adsorption. II. G. H. Coleman and C. M. McCloskey (*J. Amer. Chem. Soc.*, 1943, **65**, 1588—1594; cf. A., 1942, II, 395).—Some esters of sugars and $ArN_2{\cdot}C_6H_4{\cdot}CO_2H$ etc. are separated by chromatography on magnesite, dicalite, or SiO_2 gel. It is usually best to separate mixtures first into groups (mono-, di-saccharides etc.) and then to treat these groups on fresh columns. The following are prepared by RCOCl in C_5H_5N at 0°, room temp., or 90°: α-, m.p. 265—266°, $[\alpha]$ +223°, and β-D-*glucose* (**I**), m.p. 252—253°, $[\alpha]$ −50°, α- (**II**), m.p. 275—276°, $[\alpha]$ +436°, and β-D-*galactose* (**III**), m.p. 255—255·5°, $[\alpha]$ +170°, *penta*-p-*benzeneazobenzoate*; β-D-*fructose*, m.p. 124·5—125·5°, $[\alpha]$ −440°, α-D-*xylose*, m.p. 156—157°, $[\alpha]$ +244°, β-D- (**IV**), m.p. 261·5—262°, $[\alpha]$ −755°, and β-L-*arabinose* (**V**), m.p. 262—262·5°, $[\alpha]$ +755°, *tetra*-p-*benzeneazobenzoate*; *sucrose*, m.p. 125—125·5°, $[\alpha]$ +35°, αα- (**VI**), m.p. 134—134·5°, $[\alpha]$ +210°, and ββ-*trehalose* (**VII**), m.p. 328—329°, $[\alpha]$ +17°, α-, sinters 265°, m.p. 287—288°, $[\alpha]$ +320°, and β-*lactose*, m.p. 199—204° $[\alpha]$ +167°, α-*gentiobiose*, m.p. 232—233°, $[\alpha]$ +62°, β-*maltose*, m.p. 274—275°, $[\alpha]$ +2°, β-*cellobiose* (**VIII**), sinters 268°, m.p. 272—273° $[\alpha]$ +105°, β-*melibiose*, m.p. 279·5—280°, $[\alpha]$ +172°, *melezitose*, sinters 127—130°, $[\alpha]$ +188°, and *raffinose*, m.p. 143—145°, $[\alpha]$ +146°, *octa*-(? *hepta*-)p-*benzeneazobenzoate* ([α] above are $[\alpha]_{6438}$); *diisopropylideneglucose*, m.p. 111—112°, $[\alpha]_{6438}^2$ −81·5°, -*galactose*, m.p. 124·5—126°, $[\alpha]_{6438}$ −57°, and -*mannose* p-*benzeneazobenzoate*, m.p. 190·5—191°, $[\alpha]_{6438}$ +19°; iso*propylideneglucose tri*-p-*benzeneazobenzoate*, m.p. 166—166·5°, $[\alpha]_{6438}$ −352°; *methyl*-α-D-*glucoside*, m.p. 214—215°, $[\alpha]_{6438}^{21}$ +74°, and -*cellobioside tetra*-p-*benzeneazobenzoate*, m.p. 282—284°, $[\alpha]_{6438}^{17}$ +209°. Tetra-acetylglucosyl or hepta-acetylcellobiosyl bromide with *p*-$PhN_2{\cdot}C_6H_4{\cdot}CO_2Ag$ in C_6H_6 gives β-D-*glucose* 2 : 3 : 4 : 6-*tetra-acetate* 1-p-*benzeneazobenzoate* (**IX**), m.p. 214—215°, $[\alpha]_{6438}^{23}$ −63°, and β-*cellobiose hepta-acetate* p-*benzeneazobenzoate* (**X**), m.p. 282—284°, $[\alpha]_{6438}^{23}$ −54·5°. $[\alpha]$ are in $CHCl_3$. M.p. (above) are corr. *p*-$NH_2{\cdot}C_6H_4{\cdot}CO_2H$ and *p*-$C_6H_4I{\cdot}NO$ in EtOH–AcOH give p-p′-*iodobenzeneazobenzoic acid*, m.p. 332—334°, the chloride (prep. by $SOCl_2$), m.p. 170—171°, from which in C_5H_5N gives the *Me* ester, *anhydride*, m.p. 199—200°, and D-*glucose penta*-p-p′-*iodobenzeneazobenzoate*. The following groups are separated: (**VIII**)–(**IX**); (**II**)–(**III**); (**VI**)–(**VII**); (**IV**)–(**V**); (**I**)–(**VI**)–(**VIII**); (**V**)–(**I**)–(**VI**)–(**VIII**). R. S. C.

Action of diazomethane on acyclic sugar derivatives. V. Halogen derivatives. M. L. Wolfrom and R. L. Brown (*J. Amer. Chem. Soc.*, 1943, **65**, 1516—1521; cf. A., 1943, II, 294).—1-Diazo-1-deoxy-(**I**) with HCl–$COMe_2$–Et_2O gives 1-*chloro*-keto-D-*galaheptulose penta-acetate, forms*, m.p. 89—90° and 101—102°, $[\alpha]_D^{24}$ −32·8°, and thence (NaI–$COMe_2$) the 1-*I*-compound (**II**), m.p. 144—146°, $[\alpha]_D^{26}$ −44·8°. With the acetate of the appropriate acid in boiling C_6H_6, (**I**) gives keto-D-*galaheptulose* 2 : 3 : 4 : 5 : 6-*penta-acetate* 1-(D-*galactonate penta-acetate*), m.p. 165—167° (soft glass), 171·5—172·5° (Pyrex glass), $[\alpha]_D^{31}$ +13·0°, 1-(D-*gluconate penta-acetate*), m.p. 112—113°, $[\alpha]_D$ +22·0°, and 1-(D-*arabonate tetra-acetate*), m.p. 153—155° (soft glass), 155·5—156·5° (Pyrex), $[\alpha]_D^{32}$ +22·5°. With I in EtOH in light, (**I**) gives 1 : 1-*di-iodo*keto-D-*galaheptulose penta-acetate* (**III**), m.p. 160—163°, $[\alpha]^{19}$ +13°. 47% HI reduces (**I**), (**II**), or (**III**) exothermally to 1-*deoxy*keto-D-*galaheptulose penta-acetate, forms*, m.p. 65·5—67·5° and 78—79°, $[\alpha]_D^{28}$ −14° (*X*-ray diagrams given; *oxime*,

m.p. 125·5—126·5°, $[\alpha]_D^{28}$ +28°). 1-*Iodo*keto-D-*glucoheptulose penta-acetate*, m.p. 79—81°, $[\alpha]_D^{25}$ −9·9°, and *-fructose tetra-acetate*, m.p. 55—56°, $[\alpha]_D^{21\cdot5}$ +63°, 1-deoxy*keto*-D-fructose tetra-acetate, m.p. 81—83° (lit. 77—78°), $[\alpha]_D^{20}$ +56°, and 1-*bromo*keto-D-*galaheptulose penta-acetate*, m.p. 124—125°, $[\alpha]_D^{28}$ −36°, are similarly prepared. COPhMe is obtained from COPh·CHN_2 by 47% HI. The following revised data are recorded (cf. A., 1942, II, 395): 1-chloro-, $[\alpha]_D^{28}$ −2·8°, and 1-bromo-*keto*-D-glucoheptulose penta-acetate, m.p. 87—88°, $[\alpha]_D^{28}$ −5·5°, and 1-bromo*keto*-D-fructose tetra-acetate, m.p. 67—68°, $[\alpha]_D^{21}$ +65°. [α] are in $CHCl_3$. R. S. C.

Lead tetra-acetate oxidations in the sugar group. IV. Rates of oxidation of trehalose, β-glucosan, α-methyl-*L*-sorbopyranoside, polygalitol, and styracitol in glacial acetic acid. R. C. Hockett, (Miss) M. T. Dienes, and H. E. Ramsden (*J. Amer. Chem. Soc.*, 1943, **65**, 1474—1477; cf. A., 1943, II, 219).—The following rules are postulated: (*a*) ⩽2 $Pb(OAc)_4$ are consumed by a vicinal triol; consumption after 2 mols. is often rapid owing to side-reactions, *e.g.*, HCO_2H; (*b*) *cis*-groups are most rapidly oxidised; (*c*) OH·CHR·CHO is attacked, but often slowly; (*d*) OH·CHR·CHO is more rapidly oxidised if a γ- or δ-OH permits formation of a hemiacetal which simulates an αβ-glycol. The oxidation curves of β-methyl-*D*-xylo- and -gluco-pyranoside, β-glucosan, trehalose, α-methyl-*L*-sorbose and -*D*-gluco-pyranoside resemble each other, but differ from those of α-methyl-*D*-mannopyranoside and styracitol (**I**), which in turn are similar; that of polygalitol is intermediate between the two types. The evidence favours the 1 : 5-mannitan structure for (**I**). R. S. C.

Preparation of δ-primaverose and β-vicianose hepta-acetates. C. M. McLoskey and G. H. Coleman (*J. Amer. Chem. Soc.*, 1943, **65**, 1778—1780).—Passing HBr into xylose tetra-acetate in Ac_2O and keeping at room temp. gives β-*D*-xylosyl bromide 2 : 3 : 4-triacetate (88—90%), m.p. 98—99°, which with β-*D*-glucose 1 : 2 : 3 : 4-tetra-acetate, Ag_2O, "Drierite," and I in $CHCl_3$ gives 57% of β-primaverose hepta-acetate, m.p. 216—217° (corr.), $[\alpha]_D^{24}$ −26·2° in $CHCl_3$. β-*L*-Arabinosyl bromide triacetate gives similarly β-vicianose hepta-acetate (34%), m.p. 158—159° (corr.), $[\alpha]_D^{24}$ +9·4° in $CHCl_3$, and a substance, m.p. 144—149°. R. S. C.

Emulsin. XLIII. Fermentative fission of diglucosides of protocatechualdehyde. B. Helferich and R. Griebel (*Annalen*, 1940, **544**, 191—205; cf. A., 1940, II, 67).—Diglucosides derived from protocatechualdehyde 4-glucoside (**I**) and 4-β-d-*galactoside* (**II**) (see below) are relatively very slowly hydrolysed by emulsin from almonds or lucerne. The tetra-acetate of (**I**) with acetobromo*iso*rhamnose and NaOH in H_2O–$COMe_2$ at room temp. gives *protocatechualdehyde* 4-β-d-*glucoside* 3-β-d-iso*rhamnoside hepta-acetate* (~29%), m.p. 195—196·5°, $[\alpha]^{19}$ −56·2° in $CHCl_3$, converted by boiling NaOMe–MeOH into *protocatechualdehyde* 4-β-d-*glucoside* 3-β-d-iso*rhamnoside* (~92%), +EtOH and anhyd., m.p. 158—160°, $[\alpha]_I^{18}$ (anhyd.) −115·3° in H_2O. Similarly are prepared the 4-β-d-*glucoside tetra-acetate* 3-β-d-*glucoside* 2′ : 6′-*diacetate* 3′-*methanesulphonate* (~24%), m.p. 128·5—129°, $[\alpha]_D^{18}$ −80·4° in $CHCl_3$, converted by Ac_2O–C_5H_5N into the *hepta-acetate*, m.p. 186°, $[\alpha]_D^{18}$ −74·9° in $CHCl_3$), and thence (1% MeOH–NaOMe in $CHCl_3$ at −20°; 90 min.) the 4-β-d-*glucoside* 3-β-d-*glucoside* 2′-*acetate* 3′-*methanesulphonate* (~60%), +4H_2O and anhyd., m.p. 89°, $[\alpha]_D^{19}$ −73·1° in H_2O (complete deacetylation could not be achieved). 3 : 4 : 1-OAc·C_6H_3(OH)·CHO, acetobromogalactose (**III**), and NaOH in aq. $COMe_2$ at room temp. give *protocatechualdehyde* 3-*acetate* 4-β-d-*galactoside tetra-acetate* (~33%), m.p. 141·5—142·5°, $[\alpha]_D^{21}$ −2·96° in $CHCl_3$, and thence (NaOH–H_2O–MeOH–N_2 at room temp.) (**II**) (~58%), m.p. 178·5°, $[\alpha]_D^{20}$ −71·4° in H_2O, $[\alpha]^{19}$ −122° in 0·5N-NaOH. 3 : 4 : 1-$(OH)_2C_6H_3$·CHO with (**III**) and NaOH in aq. $COMe_2$ at room temp. gives, according to the relative amounts, the 4-β-*d*-galactoside tetra-acetate (**IV**), a syrup [hydrolysed to (**II**)], or the 3 : 4-*di*-β-*galactoside octa-acetate* (~51%), m.p. 149·5°, $[\alpha]_D^{19}$ −37·3° in $CHCl_3$, and thence (NaOMe–MeOH) the 3 : 4-*di*-β-*galactoside* (~61%), m.p. 239—241°, $[\alpha]_D^{19}$ −85·6° in H_2O. (**IV**) yields, as above, *protocatechualdehyde* 4-β-d-*galactoside tetra-acetate* 3-β-d-*glucoside triacetate* -*methanesulphonate* (~61%), m.p. 187·5—188°, $[\alpha]_D^{21}$ −43·4° in $CHCl_3$, and thence (NaOMe–MeOH–$CHCl_3$) the 4-β-d-*galactoside* 3-β-d-*glucoside* 6″-*methanesulphonate* (~82%), +H_2O and anhyd., m.p. 146—148°, $[\alpha]_D^{20}$ (anhyd.) −99·2° in H_2O. Similarly are prepared *protocatechualdehyde* 4-β-d-*lactoside*, m.p. 215—220° (decomp.), $[\alpha]_D^{21}$ −62·0° in H_2O, $[\alpha]_D^{22}$ −105° in 0·5N-NaOH [*hepta-acetate* (**V**), m.p. 203—207° (decomp.), $[\alpha]_D^{24}$ −29·8° in $CHCl_3$], 4-β-d-*lactoside* 3-β-d-*glucoside*, +H_2O and anhyd., m.p. 235—237°, $[\alpha]_D^{20}$ (anhyd.) −81·7° in H_2O (undeca-acetate, amorphous, softens 112—114°, $[\alpha]_D^{19}$ −55·4° in $CHCl_3$), and 3 : 4-*di*-β-d-*lactoside*, hygroscopic, m.p. ~200 (decomp.), $[\alpha]_D^{20}$ −60·1° in H_2O (*tetradeca-acetate*, amorphous, softens 126—129°, $[\alpha]_D^{20}$ −52·9° in $CHCl_3$). Vanillin yields similarly *vanillin* 3-β-d-*lactoside*, m.p. 228° (decomp.), $[\alpha]_D^{20}$ −53·2° in H_2O [*hepta-acetate*, m.p. 143·5—145°, $[\alpha]_D^{20}$ −38·9° in $CHCl_3$, also obtained from (**V**) (proof of structure) by CH_2N_2 or Me_2SO_4]. PhOH gives *Ph* β-d-*lactoside*, m.p. 190·5—191·5°, $[\alpha]_D^{19}$ −36·3° in H_2O (*hepta-acetate*, m.p. 161·5°, $[\alpha]_D^{20}$ −23·2° in $CHCl_3$). M.p. are corr. R. S. C.

Acid hydrolysis of *dl*-alkyl-β-*d*-glucosides.—See A., 1944, I, 19.

Fructose anhydrides. XXIII. Phlein. Ring-structure of polyfructosans. XXIV. Group of natural polyfructosans. H. H. Schlubach and O. K. Sinh (*Annalen*, 1940, **544**, 101—111, 111—116; cf. A., 1940, II, 119).—XXIII. Phlein (**I**) (prep. described), $[\alpha]_D$ −50·0° in H_2O, has mol. wt. (cryoscopic in H_2O) 2480—2615, has a reduction val. (Bertrand) 0·27%, undergoes 50% hydrolysis in N-H_2SO_4 at 20° in 235 min., and with Ac_2O in warm aq. C_5H_5N gives a triacetate, m.p. 233°, $[\alpha]_D$ +20·7° in $CHCl_3$, which in dil. aq. KOH (not by Zemplen's method) regenerates (**I**) and with Me_2SO_4–30% aq. NaOH–N_2 at 55° gives a *Me*$_3$ *ether* (OMe 45·4%), m.p. 172°, $[\alpha]_D^{20}$ −57·7° in $CHCl_3$, mol. wt. (cryoscopic in C_6H_6) 3280, hydrolysed to 1 : 3 : 4-trimethylfructose containing 1·62% of dimethylfructose as sole impurity. (**I**) has thus a cyclic structure containing 15—16 fructose units united at positions 2 and 6. Inulin, α-dextrin, and glycogen also contain closed rings. "End-group" determinations are of no val. for determination of mol. wts.

XXIV. Natural polyfructosans fall into groups. The acetates of lævan, (**I**), poain, and secalin are dextrorotatory; the differences between [α] of these acetates and the respective fructosans decreases in the same order as the yield of 1 : 3 : 4-trimethylfructose, *i.e.*, with increased chain-branching; with increasing chain-branching the mol. wt. decreases and the rate of hydrolysis increases (readier fission of side-chains). The same regularities hold for inulin, asparagosin, sinistrin, and graminin, which yield 3 : 4 : 6-trimethylfructose, except that the differences between [α] of the acetates and fructosans increase with increased branching. The purity of asphodelin is open to doubt. Triticin is abnormal and probably belongs to a third type. Irisin in also abnormal. R. S. C.

Macromolecular compounds. CCXLVI. Constitution of salepmannan. E. Husemann (*J. pr. Chem.*, 1940, [ii], **155**, 246—260).—Salep powder is boiled (1 hr.) with EtOH to inactivate a degrading enzyme and the product is washed with EtOH and Et_2O and dried at 35° vac. The residue is shaken in the dark with H_2O and the somewhat turbid solution is pptd. with MeOH. The ppt. is well pressed and triturated before treatment with Et_2O, which is removed at room temp. before the final desiccation at 35—40°/vac. Salepmannan (**I**) of various degrees of degradation is obtained by alteration of the conditions of extraction without removal of the enzyme. (**I**) is a macromol. compound since nitration does not considerably alter the degree of polymerisation. Determinations of the Staudinger K_m const. from observations of η in Schweitzer's reagent or H_2O of (**I**) of osmotically determined degree of polymerisation proves the validity of the viscosity law for degrees of polymerisation between 46 and 1550 and the similar structure of all samples of (**I**). K_m of (**I**) is nearly identical with those of cellulose (**II**) and pure mannan, thereby indicating an extended, unbranched structure of (**I**) similar to that of (**II**). Fractionation proves that (**I**) is very heterogeneous. (**I**) loses solubility in H_2O when treated with alkali and acid, which results in elimination of 1 AcOH from 11 mannose mols. Attempts to prepare a sol. (**I**) by restricted acetylation were unsuccessful. H. W.

Glucan of the yeast membrane. V. C. Barry and T. Dillon (*Proc. Roy. Irish Acad.*, 1943, **49**, **B**, 177—185).—Yeast glucan (**I**) is oxidised by HIO_4, then aq. Br, or the latter alone, in similar manner to that described for laminarin (**II**) (cf. A., 1942, II, 397). and the product is boiled with aq. $H_2C_2O_4$ to give a disaccharide, which affords laminaribiosazone. The mean length of the chain of glucose units in the mol. of (**I**) is 28 units, viz., 1·75 times that of (**II**). Configuration of the glucose units is shown to be β, *i.e.*, the same as that of the units in (**II**). A. T. P.

Limit dextrins and starch. VI. Limit dextrins from potato starch by action of pancreatic amylase. VII. Difficultly hydrolysable glucosidic linkings in starch. K. Myrback, B. Örtenblad, and K. Ahlborg. VIII. Constitution of a limit dextrin. Demonstration of α-glucosidic 1 : 6-linking in dextrin and starch. K. Myrback and K. Ahlborg (*Biochem. Z.*, 1940, **307**, 49—52, 53—68, 69—78; cf. A., 1943, III, 684).—VI. Potato starch was hydrolysed by pancreatin at pH 6·8 and room temp. for 5 months. The product, treated with increasing concns. of EtOH, yielded ten fractions of decreasing P_2O_5 content (11·7—~0·1%) and mol. wt. (~1200—550) and increasing reducing power (~16—32% as glucose). Thus the greater part (probably ~75%) of the limit dextrins (**I**) consists of tetrasaccharides and the remainder of trisaccharides. Each (**I**) appears to contain one α-glucosidic 1 : 6-linking in addition to the maltose linkings.

VII. The unimol. coeff. of hydrolysis of maltose by HCl has a const. val., whilst that of sol. starch (**II**) increases during the reaction excepting towards the end, when it decreases slightly. This indicates the presence of a small no. of difficultly hydrolysable linkings in (**II**). A variety of limit (**I**) all show a marked decrease (which is the greater the lower is the mol. wt.) in the reaction const. during hydrolysis. Hence α-glucosidic linkings other than the 1 : 4 are present in (**II**) and (**I**) and it is probable that one of these abnormal linkings is present per mol. of (**I**). The enzymic hydrolysis of (**II**) and (**I**) apparently does not involve linkings other than the 1 : 4 and 1 : 6. The possibility of the presence of an *iso*maltose linking is discussed.

VIII. (I), prepared by the action of amylase on maize starch, mol. wt. ~480, [α] +124°, was repeatedly methylated and then distilled in a vac. to give a methylated trisaccharide (OMe 51·5%), [α] +136·5° in $CHCl_3$, which, on hydrolysis, gave 1 mol. of tetramethyl- and 2 mols. of trimethyl-glucose. The trimethylglucose fraction was shown by the Oldham–Rutherford method (A., 1932, 254) to consist of approx. equal parts of 2 : 3 : 4- and 2 : 3 : 6-trimethylglucose. Thus the trisaccharide contains a maltose and an *iso*maltose linking, the latter (α-glucosidic 1 : 6-linking) being present in starch to an extent of ⩽3% of the total glucosidic linkings. The trisaccharide arises from a branching of the starch mol., if Freudenberg's theory of the structure of (II) is accepted. F. O. H.

Starch–iodine complex.—See A., 1944, I, 5.

Viscosity of cellulose acetate solutions. H. Lohmann (*J. pr. Chem.*, 1940, [ii], **155**, 299—309).—Cotton linters is acetylated (Ac_2O–H_2SO_4 in AcOH) so as to give products of differing degree of polymerisation which are then partly hydrolysed (H_2SO_4–H_2O) to the $COMe_2$-sol. stage (~2·4 OAc). Determinations of η of these products (I) which have been washed acid-free by distilled or tap H_2O show a very pronounced influence of slight differences in ash content, which are generally <0·1%. These abnormalities are not observed in AcOH. For the correlation of mechanical properties of acetate silk fibres and η in $COMe_2$ it is essential that the measurements be made in very dil. solution and that dilution must be the greater as the degree of polymerisation increases. The greatest increase of η in $COMe_2$ is caused by $CaCl_2$; $SrCl_2$ has a small effect but other Ca salts, as also Mg, Al, and alkali salts, are ineffective. Increase of [$CaCl_2$] causes increase of η and increased turbidity, the effect being less marked at 40° than at 15°. The associations causing increase of η are due to subsidiary valency activities dependent on temp. The viscosity of (I) in *m*-cresol, CH_2Cl_2–EtOH (8 : 2 by vol.), $CH_2(O{\cdot}[CH_2]_2{\cdot}OH)_2$, dioxan, or COMe–EtOH is not affected by $CaCl_2$ which causes a small increase in NH_2Ph and HCO_2Et and a great increase in COMeEt, MeOAc, and $CHCl_3$–$COMe_2$ (1 : 1). A " salt effect " is not shown by solvents containing OH or OAlk but is very obvious with esters or ketones. H. W.

III.—HOMOCYCLIC.

Formation of *cyclo*propanes from monohalides. IV. Reactions of α-chloro-β-phenyl*iso*butane (neophyl chloride). F. C. Whitmore, C. A. Weisgerber, and A. C. Shabica, jun. (*J. Amer. Chem. Soc.*, 1943, **65**, 1469—1471; A., 1943, II, 21).—$CPhMe_2{\cdot}CH_2Cl$ (I) (prep. from $CH_2{:}CMe{\cdot}CH_2Cl$ by C_6H_6–H_2SO_4 at 20°; 68% yield), b.p. 97°/13 mm., reacts less readily with Na than does $CH_2Bu^{\gamma}Cl$; with 5 Na at <90° it gives $PhBu^{\gamma}$ (34·8%), 1-phenyl-1-methyl*cyclo*propane (11·9%), and $CHPh{:}CMe_2$ (13·7%). With NaEt in C_5H_{12} at −10° to 20°, (I) gives the same products and is thus more reactive than $CH_2Bu^{\gamma}Cl$ towards NaEt. These results confirm Morton's views (A., 1943, II, 114) on the Wurtz reaction. With Na (2 atoms) in liquid NH_3, (I) gives mainly $PhBu^{\gamma}$. (I) decomposes only slowly at 135°, but at the b.p., 222°/741 mm., gives $CHPh{:}CMe_2$, $CH_2{:}CMe{\cdot}CH_2Ph$, and $CH_2Ph{\cdot}CMe_2Cl$. (I) does not react with NaOEt, C_5H_5N, or Na fluorenyl. It readily gives a Grignard reagent and thence $CPhMe_2{\cdot}CH_2{\cdot}CO_2H$ (81·6%) or $CPhMe_2{\cdot}CH_2Cl$ (30·7%). R. S. C.

***cis–trans* Isomerisation and spectral characteristics of carotenoids and related compounds.** L. Zechmeister and A. Polgár (*J. Amer. Chem. Soc.*, 1943, **65**, 1522—1528).—When an all-*trans* natural carotenoid is isomerised by boiling in C_6H_{14} or by I, λ and ε of the main max. progressively decrease, but the chief effect is appearance of a max. at 320—380 mμ., the " *cis*-peak " effect. λ of this peak is 141—144 mμ. below that of the highest max. for the all-*trans*-compound for 12 C_{40}-compounds. Methylbixin and $Ph{\cdot}[CH{:}CH]_4{\cdot}Ph$ show the same phenomenon and adding I increases ε at 240—280 mμ. for vitamin-*A*. R. S. C.

Action of cold concentrated hydriodic acid on carotenes. Structure and *cis–trans* isomerisation of reaction products. A. Polgár and L. Zechmeister (*J. Amer. Chem. Soc.*, 1943, **65**, 1528—1534).—Shaking α- or β-carotene in light petroleum with 55—58% HI (freed from I) and chromatography of the products gives ⩾9% each of 5 : 6-dihydro-β- and -α-carotene, structures of which are indicated by analysis, determination of $CMe{:}$, spectroscopy, and quant. hydrogenation. The products undergo *cis*-isomerisation when boiled in light petroleum, melted, or treated with I, and six α- and six β-isomerides are characterised by absorption max. R. S. C.

***cis–trans* Isomerisation and spectral characteristics of gazaniaxanthin. Its structure.** L. Zechmeister and W. A. Schroeder (*J. Amer. Chem. Soc.*, 1943, **65**, 1535—1540).—Petals of *Gazania rigens*, R. Br., grown in S. California, yield gazaniaxanthin (I) (0·14%), lycopene (0·0435%), γ- (0·01%) and β-carotene (0·006%), lutein, and cryptoxanthin (cf. Schon, A., 1938, II, 436). (I) is $C_{40}H_{56}O$, contains 11 conjugated C:C, with O_3 gives 1 mol. of $COMe_2$, but may be dihydrorubixanthin. It is fairly stable in light petroleum at room temp., but in boiling C_6H_6 or with I isomerisation occurs and the absorption changes in the manner characteristic of C_{40}-carotenoids. R. S. C.

Preservation and utilisation of styrene. Preparation of styrene.—See B., 1943, II, 369.

Organic reactions with boron fluoride. XXVIII. Isomeric *p*-dibutylbenzenes. G. F. Hennion and L. A. Auspos (*J. Amer. Chem. Soc.*, 1943, **65**, 1603—1606; cf. A., 1943, II, 125).—PhBu with $Pr^{\alpha}COCl$ or $Pr^{\beta}COCl$ and $AlCl_3$ in CS_2 give 76—91% of n-, b.p. 138°/6 mm., sec.-, b.p. 125°/3 mm., iso-, b.p. 116°/3 mm., and tert.-*butyl*-n-*butyrophenone*, b.p. 128°/5 mm., and n-, b.p. 118°/3 mm., sec.-, b.p. 116°/3 mm., iso-, b.p. 121°/7 mm., and tert.-*butyl*-iso-*butyrophenone*, b.p. 140°/4 mm., whence Zn–Hg–H_2O–AcOH–HCl yields p-*di*-n-, m.p. −24°, b.p. 259°/745 mm., 124°/15 mm., and p-*di*-iso-*butylbenzene*, m.p. −21°, b.p. 242°/739 mm., 109°/15 mm., p-n-*butyl*-sec.-, b.p. 250°/739 mm., 117°/15 mm., -iso-, b.p. 251°/743 mm., 118°/15 mm., and -tert.-, m.p. −46°, b.p. 248°/743 mm., 116°/15 mm., p-sec.-*butyl*-iso-, b.p. 241°/739 mm., 113°/15 mm., and -tert.-, b.p. 235°/745 mm., 108°/15 mm., and p-iso*butyl*-tert.-, b.p. 239°/751 mm., 109°/15 mm., -*butylbenzene*. In presence of BF_3–H_3PO_4, $Bu^{\alpha}OH$ or $Bu^{\beta}OH$ introduces *sec.*-Bu and Bu^{γ}, respectively, into PhBu, thus giving the *as*-compounds and p-*di*-sec.-, m.p. −58°, b.p. 239°/739 mm., 108°/15 mm., and -*tert.*-butylbenzene, m.p. 77·7°, b.p. 237°/743 mm., 109°/15 mm. (lit. 225°). *n* and *d* are also given; they are low for the compounds prepared by alkylation, probably owing to presence of small amounts of *o*-isomerides. R. S. C.

Thermal decomposition of the dibromide of αaγγ-tetraphenyl-β-methylpropene. C. F. Koelsch and R. V. White (*J. Amer. Chem. Soc.*, 1943, **65**, 1639—1640).—The product from $CHPh_2{\cdot}CHMe{\cdot}CO_2Me$ and MgPhBr in boiling Et_2O with a trace of H_2SO_4 in boiling AcOH gives *αaγγ-tetraphenyl-β-methyl-*Δ^{α}*-propene* (I) (43%), m.p. 132—133°, which with CrO_3–AcOH gives, by pinacol rearrangement, *γγδδ-tetraphenyl-*n*-butan-β-one*, m.p. 118—119°. AcOH solutions of the dibromide of (I), when distilled, give 3-*phenyl*-2-*benzhydrylindene* (II) (72%), m.p. 162—163·5°, oxidised by CrO_3–AcOH at 100° to *benzophenone*-2-*acetic acid*, m.p. 130—131°. 2-Benzylideneindanone with C_6H_6 and $AlCl_3$ gives 2-*benzhydrylindanone* (74%), m.p. 109—111°, converted into (II) by MgPhBr and then 2% H_2SO_4–AcOH. 2-Phenylindane-1 : 3-dione and MgMeI–Et_2O give 2-*phenyl*-3-*methylindone* (45%), m.p. 69—71°; *o*-$C_6H_4Ph{\cdot}MgI$ gives an oil. R. S. C.

Preparation of diphenyldimethylpolyenes. K. Bernhauer and I. Skudrzyk (*J. pr. Chem.*, 1940, [ii], **155**, 310—316).—$CHPh{:}CMe{\cdot}CHO$ (p-*nitrophenylhydrazone*, m.p. 203°) and $(CH_2{\cdot}CO_2H)_2$ with PbO_2–Ac_2O at 140°, at the b.p., afford *αθ*-diphenyl-*βη*-dimethyl-$\Delta^{\alpha\gamma\epsilon\eta}$-octatetraene, m.p. 174° (cf. Kuhn *et al.*, A., 1938, II, 437). ε-Phenyl-β-methyl-$\Delta^{\beta\delta}$-pentadien-α-al, m.p. 58° [corresponding carboxylic acid, m.p. 160°; *semicarbazone*, m.p. 239° (decomp.); p-*nitrophenylhydrazone*, m.p. 212—213°], similarly yields *αμ-diphenyl-δι-dimethyl-*$\Delta^{\alpha\gamma\epsilon\eta\lambda}$*-dodecahexaene*, m.p. 217° (decomp.); the Et_2 analogue has m.p. 206—209·5°. Tiglaldehyde is obtained from MeCHO–EtCHO–1% aq. NaOH (CO_2) at 10°. A. T. P.

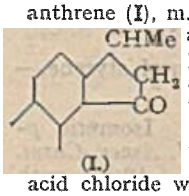
Process of obtaining α- and β-methylnaphthalene and fractions enriched in either of these compounds.—See B., 1943, II, 369.

Aromatic cyclodehydration. XII. Mechanism of the cyclisation of *o*-benzylphenones. C. K. Bradsher and E. S. Smith. **XIII. 1 : 2 : 3 : 4-Dibenzphenanthrene.** C. K. Bradsher and L. Rapoport (*J. Amer. Chem. Soc.*, 1943, **65**, 1643—1645, 1646—1647; cf. A., 1943, II, 265).—XII. α-*o*-*Chlorophenyliso*propyl *alcohol* (prep. from *o*-$C_6H_4Cl{\cdot}CO_2Me$ and MgMeI in Et_2O; 82·5% yield), b.p. 94°/8 mm., with C_6H_6 and $AlCl_3$ at <10° gives *β-phenyl-β-o-chlorophenylpropane* (61%), b.p. 146°/7 mm. With CuCN–$CH_2Ph{\cdot}CN$–C_5H_5N at 250° this gives *β-phenyl-β-o-cyanophenylpropane* (I) (68%), m.p. 62—63·5° (unaffected by boiling KOH–EtOH), and with CuCN–H_2O–C_5H_5N at 250° gives o-*aa-dimethylbenzylbenzamide* (20%), m.p. 132—134°, also obtained similarly (31%) from (I), and resistant to hydrolysis. MgPhBr and (I) in boiling C_6H_6 give o-*aa-dimethylbenzylbenzophenoneimine hydrochloride* (60%), unchanged by hot 10% HCl but in boiling 48% HBr giving 10-*phenyl*-9 ; 9-*dimethyl*-9 : 10-*dihydroanthracene* (II), m.p. 145—146° (the intermediate ketone cannot enolise). *o*-$CHPh_2{\cdot}C_6H_4{\cdot}CO_2Me$ and MgMeI give a carbinol, cyclised to (II) (proof of structure) by $AlCl_3$ in CS_2 at <10°.

XIII. Adding *o*-C_6H_4PhI and then 1-keto-1 : 2 : 3 : 4-tetrahydronaphthalene to Li in Et_2O gives 1-2′-*diphenylyl*-3 : 4-*dihydronaphthalene* (47·5%), m.p. 75·5—76·5°, which with *o*-$CO_2H{\cdot}C_6H_4{\cdot}CO_2H$ in Et_2O gives the 1 : 2-*epoxide*, m.p. 98—99°. With boiling 34% aq. HBr–AcOH this gives resinous 9 : 10-dihydro-1 : 2 : 3 : 4-dibenzphenanthrene (*picrate*, m.p. 135—136°), which with S at 200—220° and then 250° gives 1 : 2 : 3 : 4-dibenzphenanthrene, m.p. 115—116° (picrate, m.p. 139·5—140·5°; quinone, m.p. 238—240°) (cf. Hewett, A., 1938, II, 132). R. S. C.

Synthesis of 3′-alkyl-1 : 2-*cyclo*pentenophenanthrenes. B. Riegel, M. H. Gold, and M. A. Kubico (*J. Amer. Chem. Soc.*, 1943, **65**, 1772—1776).—β-2-Phenanthryl-*n*-butyric acid gives (cf. Bachmann *et al.*, A., 1940, II, 326) 1′-keto-3′-methyl-1 : 2-*cyclo*pentenophen-

anthrene (I), m.p. 135—136° [*oxime*, α-, m.p. 169—171° (decomp.), and *β-form*, m.p. 165—170° (decomp.)]. 2-Propionylphenanthrene (II) and $Al(OPr^{\beta})_3$–$Pr^{\beta}OH$ give 2-*α-hydroxy*-n-*propylphenanthrene* (73%), m.p. 87·4—88·4°, converted by PBr_3–Et_2O into the *bromide* (87·5%), m.p. 81·5—83°, which with $CHNa(CO_2Et)_2$ in $EtOH$–C_6H_6 gives *β*-2-*phenanthryl*-n-*valeric acid* (85% crude), m.p. 134·8—136·2°. The derived acid chloride with $AlCl_3$ in $PhNO_2$ at room temp.—80° gives 1′-*keto*-3′-*ethyl*-1 : 2-*cyclopentenophenanthrene* (78·5%), m.p. 110—111·2° [*oxime*, α-, m.p. 172·5—174·5° (decomp.), and *β-form*, m.p. 169—170·8° (decomp.)], reduced (Clemmensen) to 3′-*ethyl*-1 : 2-*cyclopentenophenanthrene* (94%), m.p. 85—86°, sublimes 130—140°/2—3 mm. [*picrate*, m.p. 94·8—96·4° (decomp.)]. 2-*iso*Butyrylphenanthrene yields similarly α-2-*phenanthrylisobutyl alcohol*, m.p. 104·4—104·7°, and *bromide*, m.p. 91—94° (decomp.), *β*-2-*phenanthrylisohexoic acid* (21%), m.p. 148·8—149·6° (and α-2-*phenanthrylisobutyl Et ether*, m.p. 81—83°), 1′-*keto*-3′-iso*propyl*-, m.p. 143·6—144·4° [*oxime*, m.p. 205—211° (decomp.)], and 3′-iso*propyl*-1 : 2-*cyclopentenophenanthrene*, m.p. 97·6—98·4° [impure picrate, m.p. 108—113° (decomp.), dissociates readily]. $(NH_4)_2S_x$ in dioxan at 160° and then HCl–AcOH converts (II) into *β*-2-phenanthrylpropionic acid (56·5%), m.p. 177·2—178·4°, and thence 1′-keto-1 : 2-*cyclo*pentenophenanthrene (92%), m.p. 188·6—189·4° (lit. 183—184°) [*oxime*, m.p. 235—236° (decomp.)], and 1 : 2-*cyclo*pentenophenanthrene, m.p. 134·4—135·8° [*s*-$C_6H_3(NO_2)_3$ compound, m.p. 165—167°]. 9 : 10-Dihydrophenanthrene, $R{\cdot}[CH_2]_2{\cdot}COCl$, and $AlCl_3$ in CS_2 at 0° give 2-*β-bromo*- (III), m.p. 76—77·3°, 2-*β-chloro*- (IV), m.p. 72—73°, and 2-*β-methoxy-propionyl*-9 : 10-*dihydrophenanthrene*, m.p. 87·8—88·7° [also obtained from (III) and (IV) by NaOMe–MeOH], which with chloranil in boiling xylene give only tars, although 9 : 10-dihydrophenanthrene thus gives 65% of phenanthrene (V). $Br{\cdot}[CH_2]_2{\cdot}COCl$, (V), and $AlCl_3$ in CS_2 give 2-*β-bromopropionylphenanthrene* (15%), m.p. 118·7—119·8°, reduced (Clemmensen) to 2-*n*-propylphenanthrene (picrate, m.p. 89—91°) but giving only tars when cyclised. M.p. are corr. R. S. C.

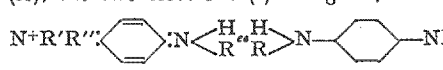


Resolutions of enantiomorphs. III. Chromatographic adsorption. H. B. Hass, T. De Vries, and H. H. Jaffé (*J. Amer. Chem. Soc.*, 1943, **65**, 1486—1488; cf. A., 1943, II, 229).—Only slight resolution of dl-α-*phenylethylamine H* d-*tartrate*, m.p. 159—162°, or brucine *dl*-mandelate occurs by adsorption on Al_2O_3, $CaSO_4$, C, fuller's earth, MgO, or glucose. R. S. C.

Selective monoreduction of aromatic dinitro-compounds by alkaline sulphides and by acid stannous chloride. H. H. Hodgson (*J. Soc. Dyers and Col.*, 1943, **59**, 246—247).—In αβ-dinitronaphthalenes, AcOH–HCl–$SnCl_2$ preferentially reduces the α-NO_2 (and ultimately produces diamines) whilst alkaline sulphides (or polysulphides) (I) reduce the β-NO_2 and then practically cease to react. This is explained on the basis of the (−*I*) inductive effect of the second nucleus (cf. A., 1938, II, 316), making the α-NO_2 more electropositive. The less positive β-NO_2 has its O atoms more available for reaction with (I). Anomalous cases are discussed. The reduction of 1 : 2 : 4-$C_6H_3Me(NO_2)_2$ at position 4- by $SnCl_2$, but at 2- by (I), and of picric to picramic acid by (I), is explained as due to the (+*I*) inductive effects of the Me and OH rendering the 2-NO_2 less positive. S. A. M.

Iodinated derivatives of sulphonamido-compounds. C. J. Klemme and E. L. Beals (*J. Org. Chem.*, 1943, **8**, 448—455).—*p*-$NHAc{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH{\cdot}CH_2{\cdot}CO_2H$ is hydrolysed by 5N-HCl and then added dropwise to ICl in hot 5N-HCl, giving 3 : 5-*di-iodosulphanilylglycine*, m.p. 249·5° (decomp.); this is diazotised and converted by KI into 3 : 4 : 5-*tri-iodobenzenesulphonylglycine*, m.p. 279—280° (decomp.). p-*Iodobenzenesulphonylglycine* has m.p. 189—191° (decomp.). *p*-$NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH{\cdot}C_6H_4{\cdot}SO_3H$-*p* is converted by ICl in 10% HCl at 40—50° into *N*-3 : 5(?)-di-iodosulphanilylsulphanilic acid, isolated as the *K* salt (anhyd. and $+2H_2O$), which is converted by diazotisation and treatment with KI into N-3 : 4 : 5-*tri-iodobenzenesulphonylsulphanilic acid*, m.p. >310°. p-$NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH{\cdot}C_6H_4{\cdot}CO_2H$, m.p. 201°, in AcOH is transformed by ICl in 10% HCl at 80—90° into p-3′ : 5′(?)-*di-iodosulphanilamidobenzoic acid*, m.p. 261·1° (decomp.), and by diazotisation followed by KI into p-*iodobenzenesulphonamidobenzoic acid*, m.p. 265—267° (decomp.). Addition of ICl in 25% HCl to $NH(SO_2{\cdot}C_6H_4{\cdot}NH_2)_2$ gives 3 : 5 : 3′-*tri-iodosulphanilamide*, m.p. 249·2° (decomp.) (*Na* salt), whereas use of the reagents in the reverse order gives this compound with the 3 : 5 : 3′ : 5′-I_4-derivative, m.p. 259—260° (decomp.; darkens at 230°) (NH_4 salt). *K* 4 : 4′-*diiododibenzenesulphonamide* is described. 2-3′ : 5′-*Di-iodosulphanilamidopyridine* has m.p. 269—272° (decomp.). H. W.

Polymerisation of free radicals of the Wurster dye type. Dimeric resonance bond. L. Michaelis and S. Granick (*J. Amer. Chem. Soc.*, 1943, **65**, 1747—1755).—Prep. of six Wurster dyes, obtainable cryst. only as bromides or perchlorates, is described. Change of colour with temp. is observable with yellow or red, but not with blue, dyes. The dyes exist in equilibrated mono- and di-meric forms in solution, but for solids there is an "all or none" law: crystals are either completely polymerised and diamagnetic with the susceptibility of an ordinary org. mol. or are completely in the free radical state and paramagnetic with the susceptibility of an org. mol. with one odd electron. The latter is so only for Wurster blue. Dimers have the structure (*A*), the two electrons (*e*) being shared between the two



(*A.*)

N, and the H and R forming a square in a plane perpendicular to the plane of the rings; resonance consists in alternation of the two rings between the quinonoid and benzenoid states. Such dimers can exist so long as at least one H is present on a N. Higher polymers can be formed along similar lines. R. S. C.

Evidence for the sulphite and sulphonate structures of Hantzsch's potassium benzene -*syn*- and -*anti*-diazosulphonates. H. H. Hodgson and E. Marsden (*J.C.S.*, 1943, 470—472).—Hantzsch's *syn*-formula for K benzene-*syn*-diazosulphonate is incorrect, and a sulphite structure, viz., $NPh{:}N{\cdot}O{\cdot}SO_2K$ or $N_2Ph\}\bar{O}{\cdot}\bar{S}O_2K$, or an equilibrium of both, accounts for all its reactions; the *anti*-form of Hantzsch is valid. The *syn*-form (I) is rapidly converted by moisture into the *anti*-form. Thus, (I) and excess of alkaline β-$C_{10}H_7{\cdot}OH$ give $PhN_2{\cdot}C_{10}H_6{\cdot}OH$-β (II), corresponding to 77·5% of *syn* + 22·5% of *anti*; a delay of 15 min. before coupling causes a decrease in *syn*-form to 33%. Coupling of (I) with *p*-$NO_2{\cdot}C_6H_4{\cdot}N_2Cl$ (III) yields a complex, converted by alkaline β-$C_{10}H_7{\cdot}OH$ into (II) + *p*-nitrobenzeneazo-β-naphthol (IV); oxidation of the filtrate affords a similar mixture. (III) combines at the S to give a N–S linking, and does not form a diazonium salt. Complexes prepared from both *syn*- and *anti*-isomerides by coupling with ArN_2Cl are unstable, except that from K benzene-*anti*-diazosulphonate (does not couple with β-$C_{10}H_7{\cdot}OH$) and (III); coupling with β-$C_{10}H_7{\cdot}OH$ then gives (IV). The complex from Na *p*-nitrobenzene-*anti*-diazosulphonate and PhN_2Cl at 0°, couples with β-$C_{10}H_7{\cdot}OH$ to give (II), whereas (IV) is obtained from the filtrate after air oxidation. The *syn*-isomeride (V), prepared from neutral (III) and Na_2SO_3 at 0°, similarly yields (II) + (IV), also obtained from the filtrate after oxidation. (V) and (III) afford a complex, and thence almost pure (IV). A. T. P.

Diphenyl series. III. Attempted chlorination of the acetate, benzoate, and benzenesulphonate of 4-chloro-4′-hydroxydiphenyl. 3 : 4′-Dichloro-4-hydroxydiphenyl. (Miss) C. M. S. Savoy and J. L. Abernethy (*J. Amer. Chem. Soc.*, 1943, **65**, 1464—1465; cf. A., 1943, II, 88).—*p*-$C_6H_4Cl{\cdot}C_6H_4{\cdot}OH$-*p* (I) and Cl_2 in CCl_4 give 3 : 4′-*dichloro*-4-*hydroxydiphenyl* (92%), m.p. 71—72° (*acetate*, m.p. 74·5—75°; *benzoate*, m.p. 125—126°; *benzenesulphonate*, m.p. 100—101°), converted by more Cl_2 in CCl_4 into 4 : 3 : 5-$OH{\cdot}C_6H_2Cl_2{\cdot}C_6H_4Cl$-*p*, which is also obtained directly from (I). Esters of (I) are unaffected by Cl_2–I (trace) in CCl_4. R. S. C.

Preparation of 4-halogeno- and 4-nitro-2-naphthols; resonance structure of the internal diazo-oxides (diazonaphthols). H. H. Hodgson and S. Birtwell (*J.C.S.*, 1943, 468—469).—Decomp. of 4-halogenonaphthalene-1 : 2-diazo-oxides (I) by Al powder in boiling EtOH (cf. Morgan *et al.*, *J.C.S.*, 1919, **115**, 1126) gives 4 : 2-$C_{10}H_6Hal{\cdot}OH$ (II). Thus prepared are 4-*chloro*-2-*naphthol* (84%), m.p. 100° (*Me ether*, m.p. 44—45°; *acetate*, m.p. 56°; 1-*benzeneazo*-derivative, m.p. 165°), 4 : 2-$C_{10}H_6Br{\cdot}OH$ (77%) (*Me ether*, m.p. 64°; *acetate*, m.p. 61°; 1-*benzeneazo*-derivative, m.p. 160°), and 4-*iodo*-2-*naphthol* (60%), m.p. 128·5° (*Me ether*, m.p. 67°; *acetate*, m.p. 59°; 1-*benzeneazo*-derivative, m.p. 176°). (I) with $SnCl_2$–aq. NaOH at 80—90° gives variable yields of (II). Attempts to prepare (II) from 4 : 2-$C_{10}H_6Hal{\cdot}NH_2$ failed. 4-Nitronaphthalene-1 : 2-diazo-oxide and Fe–$CuSO_4$–EtOH–H_2O give 50% of 4 : 2-$NO_2{\cdot}C_{10}H_6{\cdot}OH$. The properties of diazonaphthols indicate that they are resonance hybrids. A. T. P.

Synthetic œstrogenic compounds. I. Monosubstituted derivatives of αγ-di-*p*-hydroxyphenylpropane. A. H. Stuart and R. C. Tallman (*J. Amer. Chem. Soc.*, 1943, **65**, 1579—1581).—The rat unit of œstrogenic activity for $Ar{\cdot}[CH_2]_2{\cdot}CHRAr$ and $CHR(CH_2Ar)_2$ (Ar = *p*-$OH{\cdot}C_6H_4$) is 5—10 mg., a slight max. appearing at R = Pr^{α} and Et, respectively. Introduction of R has little effect. Adding *p*-$OMe{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CO{\cdot}C_6H_4{\cdot}OMe$-*p* to MgRHal (3 mols.) in Et_2O at −5° to −10° and keeping at room temp. gives p-*methoxy*-β-p-*anisyl*-n-*butyro*-, m.p. 72° (*semicarbazone*, m.p. 142—143°), -n-*valero*-, m.p. 70° (*semicarbazone*, m.p. 127—128°), -n-, m.p. 78—79° (*semicarbazone*, m.p. 126—127°), and -iso-*hexo*-, m.p. 51—52° (*semicarbazone*, m.p. 166—168°), -n-*hepto*-, m.p. 59° (*semicarbazone*, m.p. 125—127°), and -n-*octo*-*phenone*, m.p. 70°, p-*methoxy*-β-*phenyl*-β-p-*anisylpropiophenone*, m.p. 88°, p-*methoxy*-γ-*phenyl*-β-p-*anisyl*-n-*butyrophenone*, m.p. 102° (*semicarbazone*, m.p. 146°), and p-*methoxy*-ββ-*di*-p-*anisylpropiophenone*, m.p. 83—84° (*semicarbazone*, m.p. 161—162·5°). Reduction, best by H_2–Cu chromite in EtOH at 200°/~150 atm., gives αγ-*di*-p-*anisyl*-n-*butane*, b.p. 152—154°/1 mm., -n-*pentane*, b.p. 161—163°/1 mm., -n-*hexane*, b.p. 198—200°/3 mm., -δ-*methyl*-n-*pentane*, b.p. 178—179°/2 mm., -n-*heptane*, b.p. 201—203°/3 mm., and -n-*octane*, b.p. 194—195°/2 mm., β-*phenyl*-αγ-*di*-p-*anisylpropane*, m.p. 63°, δ-*phenyl*-αγ-*di*-p-*anisyl*-n-*butane*, m.p. 36—38°, and αβγ-*tri*-p-*anisylpropane*, m.p. 62—63°, demethylated

(AcOH–57% HI or EtOH–KOH) to *αγ-di-*p-*hydroxyphenyl*-n-*butane*, a resin, -n-*pentane*, m.p. 99—100°, -n-*hexane*, m.p. 101°, *-δ-methyl*-n-*pentane*, -n-*heptane*, and -n-*octane*, resins, *β-phenyl-αγ-di*-p-*hydroxyphenylpropane*, m.p. 105—106°, and *δ-phenyl-αγ-di*-p-*hydroxyphenyl*-n-*butane*, m.p. 108—110°. *p*-OMe·C_6H_4·CHO, *p*-OMe·C_6H_4·COR (improved prep. for R = Pr^a and Bu^a), and HCl at ~15° give p-*anisyl α-methyl*-, m.p. 60°, *α-ethyl*-, b.p. 200—203°/1·5 mm., and *α*-n-*propyl*-p-*methoxystyryl ketone*, b.p. 207—208°/2 mm., converted as above into CHR(CH_2·C_6H_4·OMe-*p*)$_2$ in which R = Me, m.p. 68—69°, *Et*, m.p. 43°, and Pr^a, b.p. 181°/2 mm., and thence into CHR(CH_2·C_6H_4·OH-*p*)$_2$ in which R = Me, m.p. 130°, *Et*, m.p. 102°, and Pr^a, m.p. 118—119°. R. S. C.

Analogues of hexœstrol. B. R. Baker (*J. Amer. Chem. Soc.*, 1943, **65**, 1572—1579).—The $(NH_2)_n$, $(CH_2Ph)_2$, and three steric analogues of hexœstrol are pharmacologically inactive [denoted (*I*) below]. The 3 : 4 : 3′ : 4′-$(OH)_4$-analogue is feebly active. *p*-OMe·C_6H_4·CO·CH:CH·C_6H_4·OMe-*p* and H_2–Raney Ni in EtOH at 55°/2—3 atm. give *p*-OMe·C_6H_4·CO·$[CH_2]_2$·C_6H_4·OMe-*p*, m.p. 40—42°, which with $MgPr^aBr$ in boiling Et_2O and then $KHSO_4$ at 100—120° gives *αγ-di*-p-*anisyl-Δβ*-n-*hexene* (88%), b.p. 188—190°/1 mm., reduced as above to *αγ*-di-*p*-anisyl-*n*-hexane, b.p. 178—180°/1 mm.; 48% HBr in boiling AcOH then yields *αγ*-di-*p*-hydroxyphenyl-*n*-hexane (*I*) (61%), m.p. 101·5—103° (*di*-p-*nitrobenzoate*, m.p. 114—116°). Reduction of RCO·$[CH_2]_4$·COR to R·$[CH_2]_6$·R (R = anisyl) is best (82%) effected by N_2H_4 in boiling EtOH followed by KOH on the product at 140° and finally 200°. 3 : 4-*Dimethoxypropiophenoneazine*, m.p. 151—153°, with H_2–$PdCl_2$–AcOH–MeOH gives the oily H_4-azine, which with $CuSO_4$, NaOH, and air gives the H_2-azine, converted in boiling xylene into *γδ-di*-3 : 4-*dimethoxy*- (19·5%), *forms*, m.p. 102—105° and 133—133·5°, and thence *γδ-di*-3 : 4-*dihydroxy-phenyl*-n-*hexane* (**I**) m.p. 231—235°. 50-μg. doses of (**I**) cause 100% response in ovariectomised rats, 20-μg. doses cause 29% response. p-*Propionamidopropiophenoneazine*, m.p. 276—280°, gives similarly the *H₂-azine* (18%), m.p. >160° (decomp.), which at 180° and then 240° gives *γδ-di*-p-*propionamidophenyl*-n-*hexane*, meso-, m.p. 261—264°, and dl-, m.p. 207—215°, *-forms*. Boiling conc. HCl then gives *γδ-di*-p-*aminophenyl*-n-*hexane*, meso-, m.p. 132—134°, and dl-, m.p. 63—65°, *-forms*, respectively, the configuration of which is determined by converting the former by HNO_2 into *meso*-hexœstrol. *m*-C_6H_4Et·OR (R = H or Me) with HCl–$Zn(CN)_2$–$AlCl_3$–C_6H_6 gives 4-*hydroxy*- (**II**), m.p. 51—53°, b.p. 140—145°/1 mm., and 4-*methoxy*-2-*ethylbenzaldehyde*, b.p. 133—134°/12 mm., and the derived *azines*, m.p. 204·5—206° and (**III**) 117—118° [also obtained from (**II**) by Me_2SO_4–KOH–H_2O–MeOH followed by N_2H_4], respectively. (**III**) yields the *H₂-azine*, m.p. 70—73°, and thence *αβ-di*-4-*methoxy*- (8%), m.p. 60—62°, and -4-*hydroxy*-2-*ethylphenylethane* (*I*), m.p. 131—133°. *β-Nitro-α*-p-*anisyl-Δᵅ-butene* (prep. from ArCHO, Pr^aNO_2, and OH·$[CH_2]_2$·NH_2 at room temp.; 64%), m.p. 55—57°, with $FeCl_3$–Fe in boiling HCl–EtOH–H_2O gives *p*-OMe·C_6H_4·CH_2·COEt (**IV**), b.p. 142—147°/13 mm. [semicarbazone, m.p. 153—154° (lit. 156—157°)], and thence the *dihydroazine*, m.p. 89—90°, pyrolysis of which was unsuccessful. CN·CH_2·CO_2Et, (**IV**), NH_4OAc, and AcOH in boiling C_6H_6 with removal of H_2O give *Et α-cyano-β*-p-*methoxybenzyl-Δᵅ-pentenoate*, b.p. 167—168°/1 mm., reduced (H_2–PtO_2–MeOH; 2—3 atm.) to *Et α-cyano-β*-p-*methoxybenzyl*-n-*valerate* (**V**), b.p. 158—159°/1 mm. NaOEt–EtBr in EtOH–C_6H_6 then gives *Et α-cyano-β*-p-*methoxybenzyl-α-ethyl*-n-*valerate*, b.p. 176—178°/2 mm., converted by KOH in diethylene glycol at 135—140° and then decarboxylation by a trace of CuO at 200° into *γ-cyano-δ*-p-*methoxybenzyl*-n-*hexane* (94%), b.p. 135—136°/1 mm., which resists hydrolysis by acid or alkali but with *p*-OMe·C_6H_4·MgBr in Et_2O–C_6H_6 gives 57—76% of *γ*-p-*anisoyl-δ*-p-*methoxybenzyl*-n-*hexane*, b.p. 208—211°/1 mm. Clemmensen reduction then yields *γδ-di*-p-*methoxy*- (**VI**) (78%), *form*, m.p. 71—72°, b.p. 190—195°/1 mm., and thence (HI–AcOH) *γδ-di*-p-*hydroxybenzyl*-n-*hexane* (*I*), (? meso-)*form*, m.p. 156—157° [gives (**VI**)]. *p*-OMe·C_6H_4·CH_2Cl, (**V**), and NaOEt in EtOH–C_6H_6 give *Et α-cyano-αβ-di*-p-*methoxybenzyl*-n-*valerate* (77%), b.p. 225—230°/1 mm., and thence, successively, (by KOH) *αβ-di*-p-*methoxybenzyl*-n-*valeronitrile*, b.p. 214—216°/1 mm. (*dl*-form, m.p. 136—137°), (by $^{\lambda}$IgMeI–Et_2O) *γδ-di*-p-*methoxybenzyl*-n-*hexan-β-one* (89%), b.p. 213—216°/1 mm. (form, m.p. 86—88°), and (by N_2H_4–CH_2Ph·ONa–CH_2Ph·OH) (**VI**). CN·CHNa·CO_2Et and OH·CHEt·CN in EtOH at 0° and later with EtBr at the b.p. give *Et γδ-dicyano*-n-*hexane-γ-carboxylate* (52%), b.p. 135—136°/3 mm., converted by boiling 18% HCl and then AcCl into $(CHEt·CO)_2O$, b.p. 100—102°/1 mm., which with PhOMe–$AlCl_2$–C_6H_6 at 15—20° and then H_2SO_4–MeOH–C_6H_6 gives *Me β*-p-*anisoyl-α-ethyl*-n-*valerate* (91%), b.p. 150—152°/1 mm. (enol *lactone*, b.p. ~170°/1 mm.), reduced by Zn–Hg–conc. HCl–H_2O–EtMe to *γ*-p-*anisyl-αβ-diethyl-γ-butyrolactone* (70%), b.p. 143—146°/2 mm. R. S. C.

Effect of reducing agents on the autoxidation of photographic developing agents.—See A., 1944, I, 20.

Chlorination of anisole. C. Weygand [with K. Vogel] (*J. pr. Chem.*, 1940, [ii], **155**, 342—346).—PhOMe (**I**) and Cl_2 at 150—160° give products of variable Cl content; a H_2O-insol. residue is obtained consisting of $(m$-$C_6H_4Cl)_2CO_3$, formed from *m*-C_6H_4Cl·OH and *m*-C_6H_4Cl·O·CCl_3. Better results are obtained with (**I**) as vapour; thus, chlorination at 220—225° yields PhO·CH_2Cl and PhO·$CHCl_2$. In a vac. at ~122°, a low yield of product containing 8·7% Cl results. A. T. P.

Higher homologues of azo- and azoxy-phenol ethers, and *p*-alkoxybenzylideneaniline derivatives. C. Weygand and R. Gabler (*J. pr. Chem.*, 1940, [ii], **155**, 332—341).—*p*-NO_2·C_6H_4·OK and AlkBr in COMeEt (or, for higher members, *cyclo*pentanone) give *p*-NO_2·C_6H_4 Bu^a, b.p. 160—163°/7 mm., m.p. 32°, n-C_5H_{11}, b.p. 162—163°/5 mm., n-C_6H_{13}, b.p. 172—174°/5 mm., m.p. 26°, n-C_7H_{15}, b.p. 184—185°/5 mm., n-C_8H_{17}, b.p. 196—197°/5 mm., m.p. 24°, n-C_9H_{19}, b.p. 206—207°/7 mm., m.p. 20°, n-$C_{10}H_{21}$, m.p. 41°, n-$C_{11}H_{23}$, m.p. 30°, and n-$C_{12}H_{25}$ *ether*, m.p. 53°. Electrolytic reduction (Pb anode; Pb or Ni cathode) then affords the following p-*azoxyphenol dialkyl ethers* [the occurrence of cryst.-liquid phases is observed (cf. A., 1938, II, 493; 1939, II, 16), and the clarification temp. or transition points are given in parentheses]: Bu^a_2, m.p. 107° (134°, Pl form), *di*-n-*amyl*, m.p. 82° (119°, Pl), -n-*hexyl*, m.p. 81° (127°, Pl, and 72°, Bz form), -n-*heptyl*, m.p. .74° (122·5°, Pl, and 92°, Bz form), -n-*octyl*, m.p. 76° (124·5°, Pl; 106°, Bz), -n-*nonyl*, m.p. 77° (121°, Pl; 113°, Bz), -n-*decyl*, m.p. 78° (123°, Pl; 119·5°, Bz), -n-*undecyl*, m.p. 78° (120·5°, Bz), and -n-*dodecyl*, m.p. 82° (122°, Bz). (*p*-OH·C_6H_4·N:)$_2$ and aq. AlkI–KOH–MeOH afford the Et_2, m.p. 159° (150°, Pl), Bu^a_2, m.p. 135° (124°, Pl), *di*-n-*amyl*, m.p. 112° (106°, Pl), -n-*hexyl*, m.p. 102° (114°, Pl), -n-*heptyl*, m.p. 102° (109°, Pl; 97°, Bz), -n-*octyl*, m.p. 98°, -n-*nonyl*, m.p. 103° (107°, Pl; 99°, Bz), and -n-*dodecyl ether*, m.p. 106° (107°, Pl). *p*-OH·C_6H_4·CHO affords p-*OAlk*·C_6H_4·*CHO* (**I**); Alk = Bu^a, b.p. 148—149°/10 mm., n-C_5H_{11}, b.p. 145—146°/5 mm., n-C_6H_{13}, b.p. 154—155°/6 mm., n-C_7H_{15}, b.p. 162—164°/7 mm., n-C_8H_{17}, b.p. 162—163°/4 mm., n-C_9H_{19}, b.p. 181—183°/4 mm., Pr^{β}, b.p. 135—136°/16 mm., iso*amyl*, b.p. 136—137°/15 mm., and iso*hexyl*, b.p. 175—176°/15 mm. *p*-OEt·C_6H_4·NH$_2$ in EtOH then yields p-n-*propoxy*-, m.p. 125° (123·5°, Pl), -n-*butoxy*-, m.p. 105·5° (129·5°, Pl), -n-*amyloxy*-, m.p. 102·5° (119°, Pl), -*hexyloxy*-, m.p. 97·5° (122·5°, Pl), -*heptyloxy*-, m.p. 100·5° (118°, Pl), -n-*octyloxy*-, m.p. 99° (119° Pl), -*nonyloxy*-, m.p. 101·5° (115°, Pl; 84°, 104°, Bz I; 79°, Bz II), and -*hexadecyloxy-benzylidenephenetidine*, m.p. 106·5° (105·5°, Pl). Similarly prepared are pp′-n-*propoxybenzylidene*-n-*propoxy*-, m.p. 133° (calc. 107°, Pl), -n-*butoxybenzylidene*-n-*butoxy*-, m.p. 125° (121°, Pl), and -n-*amyloxybenzylidene*-n-*amyloxy-aniline*, m.p. 113° (103°, Pl), and -n-*nonyloxybenzylideneanisidine*, m.p. 108° (96°, Pl); pp′-n-*nonyloxybenzylidine-toluidine*, m.p. 73° (76°, Pl; 74°, Bz I, 70°, Bz II), *-ethylaniline*, m.p. 65° (77°, Bz I; 74°, Bz II), and -n-*propylaniline*, m.p. 51° (83°, Bz I; 79°, Bz II), and -n-*octyloxybenzylidenetoluidine*, m.p. 70° (75°, Pl; 67°, Bz I; 59°, Bz II). (**I**) and *p*-NH_2·C_6H_4·CH:CH·CO_2Et in EtOH afford *Et* p-n-*propoxy*-, m.p. 64° (159°, Bz I; 131°, Bz II), -n-*butoxy*-, m.p. 66° (162°, Bz I; 134°, Bz II), -n-*amyloxy*-, m.p. 62° (158°, Bz I; 128°, Bz II), -n-*hexyloxy*-, m.p. 49° (156°, Bz I, 126°, Bz II), and -n-*nonyloxy-benzylidene*-p-*aminocinnamate*, m.p. 74° (154°, Bz I; 116°, Bz II). A. T. P.

Condensation of *o*-cresol with formaldehyde in alkaline solution. F. Hanus (*J. pr. Chem.*, 1940, [ii], **155**, 317—331).—*o*-Cresol (1 mol.) in 10% aq. NaOH and 40% CH_2O (1 mol.) at 10—15° for 2 days give a mixture (*A*) from which 2-*hydroxy*- (**I**), m.p. 32·8—33·8°, and 4-*hydroxy*-3-*methylbenzyl alcohol*, m.p. 81—84°, are isolable. 2 Mols. of CH_2O yield 2 : 1 : 3 : 5-OH·C_6H_2Me(CH_2·OH)$_2$ (**II**) and/or di-(4-hydroxy-5-hydroxymethyl-3-methylphenyl)methane (**III**), according to conditions used. Oxidation (aq. NaOH–*m*-NO_2·C_6H_4·SO_3Na) of (*A*) gives, through the $NaHSO_3$ compounds, 2 : 1 : 3- and 2 : 1 : 5-OH·C_6H_2Me·CHO, and *o-cresol*-3 : 5-*dialdehyde* (**IV**), m.p. 122—122·6° [*dioxime*, m.p. 182—183° (sinters from 174°); also obtained by CrO_3–AcOH oxidation of (**II**)]. (**III**), also prepared from (**II**) and the calc. amount of aq. NaOH at 40°, or from (**I**) + (**II**) in 10% aq. NaOH at 15°, is oxidised by $Na_2Cr_2O_7$–AcOH to (**IV**). A. T. P.

Reaction of epichlorohydrin with the Grignard reagent. Derivatives of *cyclo*propanol. G. W. Stahl and D. L. Cottle (*J. Amer. Chem. Soc.*, 1943, **65**, 1782—1783).—Epichlorohydrin with $MgBr_2$ (1 mol.) and a trace of $FeCl_3$ and then MgEtBr (3 mols.) gives rapidly 43% of *cyclo*propanol (cf. Magrane *et al.*, A., 1942, II, 214), b.p. 100—103°, which could not be purified but is characterised as *phenyl*-, m.p. 101·5—102°, *α-naphthyl*-, m.p. 100·5—101·5°, and p-*nitrophenyl-urethane*, m.p. 159—160°, p-*nitro*-, m.p. 72—72·5°, and 3 : 5-*dinitro-benzoate*, m.p. 108—109°, and *allophanate*, m.p. 179—181° (decomp.). When kept over K_2CO_3 it gives CHEt:CMe·CHO (semicarbazone, m.p. 187—188°). R. S. C.

Lignin. XLII. [Hydrogenation of methoxyphenols.]—See A., 1943, II, 402.

Antispasmodics. V. F. F. Blicke and N. Grier (*J. Amer. Chem. Soc.*, 1943, **65**, 1725—1728).—*p*-C_6H_4Ph·CO·CO_2Et (**I**) (prep. from Ph_2 by CO,Et·COCl and $AlCl_3$ in CS_2) with boiling Na_2CO_3–H_2O–EtOH gives *p*-C_6H_4Ph·CO·CO_2H (**II**), m.p. 105—107° (lit. decomp. 170°), and with H_2–Pt (? Pd)–C in EtOH at 3 atm. and then 10% KOH–EtOH gives *p*-C_6H_4Ph·CH(OH)·CO_2H, m.p. 201—203° (lit. 192°), reduced by red P–I–AcOH to *p*-C_6H_4Ph·CH_2·CO_2H. Adding MgRBr to (**I**) in Et_2O–N_2 and then hydrolysing by 10% KOH–

EtOH gives *α-hydroxy-α-phenyl-α*-p-*xenyl-*, m.p. 168—170°, and *α-hydroxy-α*-cyclo*hexyl-α*-p-*xenyl-acetic acid*, m.p. 202—203°, and *α-hydroxy-α*-p-*xenylpropionic acid*, m.p. 168—169°. MgRBr and (**II**) in Et_2O give *α-hydroxy-α*-p-*xenyl-butyric*, m.p. 175—177°, *-n-valeric*, m.p. 142—143°, and *-n-hexoic acid*, m.p. 178—179°. Red P–I–AcOH then gives *α-phenyl-α*-p-*xenyl-*, m.p. 141—142°, and *α*-cyclo*hexyl-α*-p-*xenyl-acetic acid*, m.p. 204—205°, *α*-p-*xenyl-propionic* (**III**), m.p. 145—147°, *-n-butyric*, m.p. 123—125°, *-n-valeric*, m.p. 116—117°, and *-n-hexoic acid*, m.p. 99—101°. The following are prepared by heating the appropriate acid and aminoalkyl chloride in $PrOH$ or the appropriate acid chloride and NH_2-alcohol in C_6H_6: *β-dimethylaminoethyl*, m.p. 158—159°, *β-piperidinoethyl*, m.p. 163—164°, and *γ-diethylaminopropyl α*-p-*xenylacetate hydrochloride*, m.p. 113—115°; *β-diethylamino-*, m.p. 139—141°, *β-dibutylamino-*, m.p. 128—130°, and *β-piperidino-ethyl*, m.p. 147—149°, *γ-diethylamino-*, m.p. 117—119°, and *γ-piperidino*-n-*propyl α*-p-*phenyl-α*-p-*xenylacetate hydrochloride*, m.p. 103—105°; *β-diethylamino-*, m.p. 170—172°, and *β-piperidino-ethyl*, m.p. 179—181°, and *γ-diethylamino*-n-*propyl α*-cyclo*hexyl-α*-p-*xenylacetate hydrochloride*, m.p. 149—151°; *β-diethylamino-*, m.p. 141—143°, and *β-piperidino-ethyl*, m.p. 162—164°, *γ-diethylamino-*, m.p. 112—114°, and *γ-piperidino*-n-*propyl α*-p-*xenylpropionate hydrochloride*, m.p. 142—144°; *β-diethylamino-*, m.p. 154—156°, and *β-piperidino-ethyl*, m.p. 146—148°, and *γ-diethylamino*-n-*propyl α*-p-*xenyl*-n-*butyrate hydrochloride*, m.p. 97—99°; *β-diethylamino-*, m.p. 122—124°, and *β-piperidino-ethyl*, m.p. 127—129°, and *γ-diethylamino*-n-*propyl α*-p-*xenyl*-n-*valerate hydrochloride*, m.p. 100—102°. Of the esters, those of (**III**) are the most potent antispasmodics on the untreated, isolated intestinal strip. R. S. C.

Preparation of iodine-containing *X*-ray contrast substances. II. α-Phenyl-β-3 : 5-di-iodo-4-hydroxyphenylpropionic acid ("biliselectan"). W. Baker and (in part) H. Sansbury (*J.S.C.I.*, 1943, **63**, 191—192).—*p*-OH·C_6H_4·CHO, anhyd. $CH_2Ph·CO_2Na$, and Ac_2O at 170—180° (bath; 17 hr.) and hydrolysis (aq. EtOH–NaOH) of the product give *p*-OH·C_6H_4·CH:CPh·CO_2H (83%) (and some *p*-OH·C_6H_4·CH:CHPh), reduced in aq. NaOH–EtOH by Raney Ni and H_2 (2—3 atm.) to *p*-OH·C_6H_4·CH_2·CHPh·CO_2H (**I**) (93%). With ICl in hot aq. AcOH–HCl, this gives 4 : 3 : 5 : 1-OH·$C_6H_2I_2$·CH_2·CHPh·CO_2H (**II**), m.p. 159—160° (corr.; shrinks from ~153°), purified by pptn. of the Na salt from hot 10% NaOH by NaCl, followed by crystallisation of the acid successively from $CHCl_3$, 45% (vol.) EtOH, and 55% EtOH; overall yield 52%. It is also prepared (42% overall yield) from *p*-OMe·C_6H_4·CHO (could not be demethylated satisfactorily), which is converted into *p*-OMe·C_6H_4·CH_2·CHPh·CO_2H as above, and then demethylated with aq. HBr–AcOH to (**I**). (**II**) titrates as a dibasic acid; it is an orally-administered *X*-ray contrast substance for the gall-bladder. S. A. M.

Fluorinated compounds of possible chemotherapeutic interest. E. Bograchov (*J. Amer. Chem. Soc.*, 1943, **65**, 1652—1653). C_6H_4F·COCl and 4 : 1-PhN_2·$C_{10}H_6$·NH_2 in C_5H_5N–$CHCl_3$ at 0° give 1-o-, m.p. 154°, and 1-p-*fluorobenzamido*-4-*benzeneazonaphthalene*, m.p. 201° N⁴-o-*Fluorobenzoylsulphanilamide*, m.p. 264°, is prepared from *o*-C_6H_4F·COCl and *p*-NH_2·C_6H_4·SO_2·NH_2 in AcOH at 0°. R. S. C.

2′-Hydroxydiphenylphthalide. M. H. Hubacher (*J. Amer. Chem. Soc.*, 1943, **65**, 1655—1656).—4′-Hydroxydiphenylphthalide, new m.p. 170·1—170·4°, obtained from *o*-C_6H_4Bz·COCl and PhOH in C_6H_6 at 40°, is accompanied by a little of the 2′-*OH*-isomeride, m.p. 240·5—241·3° [separated by sublimation; *acetate*, m.p. 136·6—137·7°; Me ether, m.p. 126·1—126·7° (lit. 127—128°); with KOH at 240—245° gives 9-phenylxanthene and BzOH]. R. S. C.

Optically active acyl peroxides. Preparation, decomposition, and use as catalysts for vinyl polymerisation. C. S. Marvel, R. L. Frank, and E. Prill (*J. Amer. Chem. Soc.*, 1943, **65**, 1647—1652).—*p*-C_6H_4BrBu-*sec.* (**I**) with CuCN gives dl-p-sec.-*butylbenzonitrile* (84%), b.p. 78—80°/4 mm., hydrolysed by 75% H_2SO_4 at 150° to dl-, m.p. 93·5—94° (91—92° by Grignard method), resolved by quinine to l-p-sec.-*butylbenzoic acid* (**I**), m.p. 88·5—89°, $[\alpha]_D^{26}$ −23·5° in MeOH (*quinine* salt, m.p. 184—185°, $[\alpha]_D^{6}$ −138·4° in MeOH; impure *d*-form, $[\alpha]_D^{30}$ +18·2° in MeOH). The derived ($SOCl_2$–C_6H_5N) dl-, b.p. 135—137°/15 mm., and l-*chloride*, b.p. 143—144°/20 mm., in C_6H_6 with aq. Na_2O_2 at 0° give dl-, m.p. 49—50°, and l-p-sec.-*butylbenzoyl peroxide* (**II**), m.p. 45·5—47°, $[\alpha]_D^{27}$ −29·0° in dioxan. In dioxan at 55°, *dl-* or *l-*(**II**) decompose to give *dl-* or *l-*(**I**), respectively, but changes in [α] for *l-*(**II**) are too small for calculation of kinetics. *l*-Menthyl H phthalate, m.p. 108·5—110°, gives similarly l-o-*carbomenthoxybenzoyl peroxide*, m.p. 117—118° (decomp.), $[\alpha]_D^{27}$ −91·6° in dioxan, decomp. of which in dioxan at 55° is unimol. (k 1·15 × 10^{-4} sec.$^{-1}$; half-life 1·75 hr.). Polymerisation of styrene, CH_2:CMe·CO_2Me, or CH_2:CH·CN in presence of *l-*(**II**) discloses no peculiarity. R. S. C.

Antispasmodics. II. Basic esters of polynuclear carboxylic acids. R. R. Burtner and J. W. Cusic (*J. Amer. Chem. Soc.*, 1943, **65**, 1582—1585; cf. A., 1943, II, 161).—Of the esters described below, (**I**) and (**II**) are much the most potent antispasmodics. The following are usually prepared by LiBu$^{\alpha}$ and then CO_2 : 9 : 10-dihydroanthracene-9-, xanthene-9-, *thioxanthene*-10-, m.p. 227°, 10-*methyl*-5 : 10-*dihydroacridine*-9-, m.p. 184° (decomp.), 9-, m.p. 194—196°, and 10-*methyl*-9 : 10-*dihydroanthracene*-9-, m.p. 204—207°, and 9-cyclo*hexylfluorene*-9-*carboxylic acid*, m.p. 220—222°. The following are prepared, m.p. being those of the *hydrochlorides*: β-diethylaminoethyl (**I**), m.p. 170—171°, β-, m.p. 185°, and γ-diethylamino-*n*-propyl, m.p. 136°, β-di-*n*-butylaminoethyl, m.p. 130°, and β-morpholinoethyl 9 : 10-dihydroanthracene-9-carboxylate, m.p. 142°; di-β-diethylaminoethyl 9 : 10-dihydroanthracene-9 : 10-dicarboxylate, m.p. 192—193°; β-diethylaminoethyl 10-, m.p. 202°, and 9-methyl-9 : 10-dihydroanthracene-9-carboxylate, m.p. 157—159°, xanthene-9-carboxylate (**II**), m.p. 159—160°, thioxanthene-10-carboxylate, m.p. 195°, acridan-5-carboxylate, m.p. 201°, 10-methylacridan-5-carboxylate, m.p. 157—158°, acridine-5-carboxylate, m.p. 190° (lit. 179—180°), 9-ethyl-, m.p. 168—169°, and 9-cyclohexyl-fluorene-9-carboxylate, m.p. 184°, indene-1-carboxylate, m.p. 141—143°, 1-naphthoate, m.p. 159—161°, 1 : 4-dihydro-, m.p. 152°, and 1 : 2 : 3 : 4-tetrahydro-1-naphthoate, m.p. 137—138°, diphenylyl-2-acetate, m.p. 108—109°, and phenanthrene-9-carboxylate, m.p. 169—170° (lit. 171—171·5°). R. S. C.

Pentagallates of glucose and mannose.—See A., 1944, II, 6.

4 : 4′-Dicyanobenzaldazine. H. J. Barber and R. Slack (*J. Amer. Chem. Soc.*, 1943, **65**, 1776—1777).—Contrary to Sah (A., 1942, II, 313), *p*-CN·C_6H_4·CHO (prep. from the alcohol by N_2O_4) with N_2H_4,H_2O in EtOH gives the azine, m.p. 318—320°, which yields no (*p*-CN·C_6H_4·CH:)$_2$ but when repeatedly sublimed at 300—320° gives a small amount of *p*-$C_6H_4(CN)_2$. R. S. C.

Gattermann reaction with monomethoxydiphenyl ethers. H. E. Ungnade and E. F. Orwoll (*J. Amer. Chem. Soc.*, 1943, **65**, 1736—1739).—*o*-OMe·C_6H_4·OPh with $AlCl_3$–HCN in C_6H_6 at 0° and then 40—50° gives 40—50% of mixed aldehydes (*A*), whence $KMnO_4$–$COMe_2$ gives 4 : 3 : 1-OMe·C_6H_3(OPh)·CO_2H (**I**), m.p. 186—186·5°. 1 : 3 : 4-C_6H_3MeBr·N_2·HSO_4 with boiling aq. Na_2SO_4–H_2SO_4 gives 1 : 3 : 4-C_6H_3MeBr·OH (93—96%), b.p. 102—104°/20 mm., the Me ether, b.p. 126—127°/25 mm., of which with KOPh and Cu powder at 160—200° gives *Ph* 4-*methoxy*-m-*tolyl ether*, m.p. 38·5—39°. With HI–AcOH this gives *Ph* 4-*hydroxy*-m-*tolyl ether*, m.p. 69·5—70°, and with $KMnO_4$ in aq. C_5H_5N gives (**I**), converted by $AlCl_3$ in C_6H_6 or HBr–AcOH at 150° (not HI–Ac_2O) into 4-*hydroxy*-3-*phenoxybenzoic acid*, m.p. 187·6—188°, $AlCl_3$ in C_6H_6 converts (*A*) into 4-*hydroxy*-3-*phenoxybenzaldehyde* (**II**), m.p. 121·5—122°, and *o*-OH·C_6H_4·OPh (**III**). Me_2SO_4 converts (**II**) into 3-*phenoxy*-4-*methoxybenzaldehyde*, m.p. 49—50° [*semicarbazone*, m.p. 172·4—173°; oxidised to (**I**)]. *o*-OMe·C_6H_4·O·C_6H_4·CHO-*p* (*semicarbazone*, m.p. 207—208°) with $AlCl_3$ in C_6H_6 gives (**III**), whence its formation from (*A*) is explained. By successive treatment with HI–Ac_2O–AcOH, esterification (Ag salts), and extraction with NaOH, the acids from (*A*) give *o*-OH·C_6H_4·O·C_6H_4·CO_2H-*p* (**IV**), which is also obtained by KOH–$(CH_2$·$OH)_2$. With KOH–$(CH_2$·$OH)_2$ *o*-OMe·C_6H_4·O·C_6H_4·CO_2H-*p* gives (**IV**) (53%), but (**I**) gives (**III**) (75%). The *oxazolone*, m.p. 183·5—184°, from (**II**) gives m-*phenoxytyrosine*, m.p. 236° (block; preheated at 200°) [absorption max. at 2970 A. (log ε 3·62), min. at 2750 A. (log ε 3·4)]. The aldehyde mixture (*B*) obtained in 40—45% yield from *m*-OPh·C_6H_4·OMe (**V**) gives acids (*C*), whence H_2SO_4 gives 16·7% and AcCl gives 23% of 3-methoxyxanthone (**VI**); 2 : 4 : 1-OPh·C_6H_3(OMe)·CO_2H (**VII**) gives 84% of (**VI**). 3-Hydroxyxanthone, prepared from (**VI**) by $AlCl_3$, has m.p. 249—250° (lit. 243°). (**VII**) gives similarly 4-*hydroxy*-2-*phenoxybenzoic acid*, m.p. 163—164°. 1 : 4 : 2-C_6H_3MeCl·NH_2 (prep. from the NO_2-compound by H_2–Raney Ni in MeOH at 60°/2000 lb.), b.p. 120—125°/40 mm., gives 1 : 4 : 2-C_6H_3MeCl·OH (85%), m.p. 67—68°, the Me ether, b.p. 104—106°/25 mm., of which with KOPh and Cu powder at 250—270° gives 4 : 1 : 2-OPh·C_6H_3Me·OMe (10%), b.p. 275—276°, oxidised and then demethylated (AcOH–HI) to 2-*hydroxy*-4-*phenoxybenzoic acid* (**VIII**), m.p. 182·4—183°. (**VIII**) is obtained (m.p. 180·8—181·4°) from (*C*) by $AlCl_3$. (**V**) with KOH–$(CH_2$·$OH)_2$ or HI–AcOH gives *m*-OPh·C_6H_4·OH (oxyacetic acid *derivative*, m.p. 67—67·4°), also obtained from (*B*) by $AlCl_3$–C_6H_6. By the Gattermann synthesis *p*-OPh·C_6H_4·OMe gives 6% of *p*-OMe·C_6H_4·O·C_6H_4·CHO. R. S. C.

Formation and structure of organic molecular compounds. II. Molecular compounds of *s*-trinitrobenzene with unsaturated ketones. J. Weiss (*J.C.S.*, 1943, 462—463).—*s*-$C_6H_3(NO_2)_3$ (**I**) and unsaturated ketones with the CO forming part of the conjugated system form mol. compounds. *Compounds* with the following ketones have been prepared in EtOH, the ratio ketone : (**I**) and m.p. being indicated: $(CHPh:CH)_2CO$, 1 : 2, 127°; 2 : 1, 115°; *p*-OMe·C_6H_4·CH:CH·CO·CH:CHPh, 1 : 1, 114°, 1 : 2, 124°; (*p*-OMe·C_6H_4·CH:CH)$_2$CO, 1 : 1, 115°; 2 : 1, 122°; $(CHPh:CH·CH:CH)_2CO$, 1 : 1, 113°; 1 : 2, 110°. Compounds are not formed by ketones of the type RCOMe (R = CHAr:CH); hence it is not the isolated group R but the conjugate system as a whole that is responsible for compound formation, the link being provided by the CO. The structure of the compounds and its relation to their colour are discussed. C. R. H.

Properties of *m*-nitrodibenzoylmethane. R. P. Barnes and L. B. Dodson (*J. Amer. Chem. Soc.*, 1943, **65**, 1585—1588).—*m*-$NO_2{\cdot}C_6H_4{\cdot}COMe$, PhCHO, and NaOH in MeOH–H_2O give *m-nitrophenyl styryl ketone*, m.p. 125—127°, the *dibromide* (**I**), m.p. 162—162·3°, of which with NaOMe–MeOH and then HCl–MeOH gives an enol (**II**), $OH{\cdot}CPh{:}CH{\cdot}CO{\cdot}C_6H_4{\cdot}NO_2$, m.p. 131—134° (cf. Bodforss, A., 1917, i, 223). With NH_2OH,HCl and KOH in EtOH, (**I**) gives *5-phenyl-3-m-nitrophenylisooxazole*, m.p. 169·5—170°, also obtained from (**II**) by NH_2OH,HCl in MeOH. Similar treatment of $COPh{\cdot}[CHBr]_2{\cdot}C_6H_4{\cdot}NO_2$ gives *3-phenyl-5-m-nitrophenylisooxazole*, m.p. 180°. Warming (**I**) with $NHPh{\cdot}NH_2$ in MeOH and later warming with KOH gives 1 : 5-diphenyl-3-*m*-nitrophenylpyrazole (**III**), m.p. 131°. N_2H_4 leads similarly to 5-phenyl-3-*m*-nitrophenylpyrazole (**IV**), m.p. 206°. Incorrect configurations were previously (*loc. cit.*) assigned to (**III**) and (**IV**). R. S. C.

Condensation of ethyl methylacetoacetate with ethyl chlorofumarate. R. B. Woodward and W. A. Reed (*J. Amer. Chem. Soc.*, 1943, **65**, 1569—1572).—Contrary to Ruhemann *et al.* (*J.C.S.*, 1896, **69**, 1386; 1897, **71**, 325), Et_2 chlorofumarate and $CHMeAc{\cdot}CO_2Et$ give an enolic form of *Et*$_2$ *4-methyl-*Δ^5*-cyclohexene-1 : 3-dione-4 : 5-dicarboxylate* [absorption max. at 326 (log ε 3·68) and ~250 mμ.], converted by hot, conc. HCl into 4 : 6 : 1 : 2-$(OH)_2C_6H_2Me{\cdot}CO_2H$ and thence by conc. H_2SO_4 at 100° into 2 : 4 : 6 : 8-tetrahydroxy-1 : 5-dimethylanthraquinone (tetra-acetate, m.p. 231—232°). R. S. C.

β-Alkylation of certain cationoid systems by means of Grignard reagents. A. J. Birch and (Sir) R. Robinson (*J.C.S.*, 1943, 501—502; cf. A., 1942, II, 345).—Carvone and MgMeI–Et_2O in presence of a little CuBr, followed by heating the product with a trace of I at 180°, afford 6-methylcarvomenthone, b.p. 235—240°, with some diene, b.p. ~200°. 2-Keto-$\Delta^{1:9}$-octohydronaphthalene and MgMeI (+ CuBr) give *cis*-2-keto-9-methyldecahydronaphthalene, m.p. ~14·5°, b.p. 250—254° (2 : 4-*dinitrophenylhydrazone*, m.p. 106°; *CHPh*: derivative, m.p. 85—86°; the oxime separates as a mixture of isomerides, converted by NH_2OH,HCl–aq. EtOH in 1 week into the form, m.p. 109°), oxidised to *cis*-1-methyl*cyclo*hexane-1 : 2-diacetic acid (cf. Linstead *et al.*, A., 1937, II, 406). 2-Keto-10-methyl-$\Delta^{1:9}$-octahydronaphthalene similarly gives (?) trans-2-*keto*-9 : 10-*dimethyldecahydronaphthalene*, m.p. 90—95° (*semicarbazone*, m.p. 202—203°). Et *cyclo*hexylidenecyanoacetate and *n*-$C_{10}H_{21}{\cdot}MgBr$ or MgMeI yield *Et* 1-n-*decyl*- (14%), b.p. 230—235°/15 mm. (and some $C_{20}H_{42}$), or (after previous extraction of the product with aq. EtOH–NaCN) *Et* 1-*methyl*-cyclo*hexane*-1-*cyanoacetate* (45%), b.p. 155—160°/12 mm., respectively. The latter and 15% aq. NaOH give 1-*methyl*cyclo*hexane*-1-*malonamic acid*, m.p. 151°, converted at 180° into the -1-*acetamide*, m.p. 112—113°. 2-β-Carbethoxyethyl*cyclo*hexanone, $CN{\cdot}CH_2{\cdot}CO_2Et$, and piperidine at 100° (bath; 10 hr.) yield *Et 2-β-carbethoxyethyl-*Δ^1*-cyclohexene-1-cyanoacetate*, b.p. 150—153°/0·1 mm., which is not alkylated by MgMeI (+CuBr). A. T. P.

Structure of diketen.—See A., 1944, I, 4.

Reactions and enolisation of cyclic diketones. VII. 1 : 2-Diketo-3-*tert.*-butylhydrindene. C. F. Koelsch (*J. Amer. Chem. Soc.*, 1943, **65**, 1640—1643; cf. A., 1942, II, 23).—Enolisation of 1 : 2-*diketo*-3-tert.-*butylhydrindene* (**I**) (see below) is entirely suppressed by the Bu^γ. $CO(CH{:}CHPh)_2$ and $MgBu^\gamma Cl$ in boiling Et_2O–C_6H_6 give αε-*diphenyl-*ζζ*-dimethyl-*Δ^α*-hepten-γ-one* (**II**), m.p. 146—148°, oxidised by $KMnO_4$–$COMe_2$ or, less well, CrO_3–AcOH to *β-phenyl-γγ-dimethyl*-n-*valeric acid* (**III**), m.p. 114—116° (*anilide*, m.p. 123—125°), the chloride ($SOCl_2$) of which with $AlCl_3$ in C_6H_6 gives 3-tert.-*butyl*-1-*hydrindone*, b.p. 150—153°/20 mm. (*oxime*, m.p. 135—137°). With OBu·NO–conc. HCl–EtOH at 22—65° this gives the *2-NOH*: derivative, m.p. 182—185°, converted by CH_2O–HCl–AcOH into (**I**), m.p. 76—78° [$NaHSO_3$ compound; with *o*-$C_6H_4(NH_2)_2$ gives a *quinoxaline*, m.p. 131—132°]. Solid (**I**) is orange and its solutions in org. solvents are orange-pink; in aq. alkali it is deep blue. It is stable to air and Br–CCl_4. In aq. NaOH, H_2O_2 converts it into α-tert.-*butylhomophthalic acid*, m.p. 176—178° (gas) (*anhydride*, m.p. 106—107°). $CHPh{:}CH{\cdot}COMe$ and $MgBu^\gamma Cl$ in Et_2O give δ-*phenyl-*εε*-dimethyl*-n-*hexan-β-one* (**IV**), m.p. 61—62°, b.p. 145—150°/20 mm., and, by 1 : 2-addition, $CHPh{:}CH{\cdot}CMeBu^\gamma{\cdot}OH$ (**V**). (**V**) could not be purified nor could the dehydration product, $CHPh{:}CH{\cdot}CBu^\gamma{:}CH_2$, formed by distillation, but the presence of the latter is proved by condensation with $(CH{\cdot}CO)_2O$ at 100° to give 5-tert.-*butyl*-1 : 2 : 3 : 4-*tetrahydrodiphenyl*-2 : 3-*dicarboxylic anhydride*, m.p. 177—178°, and thence the derived *acid*, sinters 170°, m.p. 190—192° (gas) (*Ag*$_2$ salt). With S at 250° this gives 5-tert.-*butyldiphenyl*-2 : 3-*dicarboxylic* [5-tert.-*butyl*-3-*phenylphthalic*] *acid*, sinters 170°, m.p. 190—192° (gas) [*salt*, NaHX,H_2X, m.p. >270°; *anhydride*, m.p. 142—143°], which with conc. H_2SO_4 at 100° yields 3-tert.-*butyl*-9-*fluorenone*-1-*carboxylic acid*, m.p. 184—186°. Only a poor yield of (**III**) is obtained from (**IV**) by HOHal; a better yield is obtained by condensing with PhCHO to give (**II**) which is then oxidised as above. R. S. C.

Synthesis of substances related to the sterols. XLII. R. H. Martin and (Sir) R. Robinson (*J.C.S.*, 1943, 497—501; cf. A., 1941, II, 295).—3-Phenyl-Δ^2-*cyclo*pentenone-2-acetic acid and Ac_2O at 190° give 3′-*keto*-4-*acetoxy*-1 : 2-cyclo*pentenonaphthalene*, m.p. 159—160°; hydrolysis with aq. NaOH–EtOH gives the 4-OH-compound (improved prep.; cf. *loc. cit.*). The *Me ether* (**I**), m.p. 127·5—128·5° (2 : 4-*dinitrophenylhydrazone*, m.p. 301°), of this is converted by $CH_2Br{\cdot}CO_2Et$–Zn–C_6H_6 into *Et* 4-*methoxy*-1 : 2-cyclo*pentadienonaphthalene*-3′-*acetate*, m.p. 123—123·5° [free *acid*, m.p. 226—228° (decomp.)], which is reduced (H_2, 2% Pd–$SrCO_3$, MeOH at 18°/2 atm.) and then hydrolysed (KOH–MeOH–little H_2O) to 4-*methoxy*-1 : 2-cyclo*pentenonaphthalene*-3′-*acetic acid* (**II**), m.p. 136—137·5° (previous sintering). With SeO_2 in boiling AcOH (3 min.), (**I**) gives 2′ : 3′-*diketo*-4-*methoxy*-1 : 2-cyclo*pentenonaphthalene*, m.p. 178—180°. *m*-$OMe{\cdot}C_6H_4{\cdot}CO{\cdot}CHAc{\cdot}CO_2Et$ is hydrolysed (10% aq. NH_3 followed by boiling 10% aq. NaOH) to *m*-$OMe{\cdot}C_6H_4{\cdot}COMe$, which with furfuraldehyde in cold 1% MeOH–NaOMe affords *furfurylidene*-3-*methoxyacetophenone*, b.p. 175°/0·45 mm., m.p. 38·5—39·5° (2 : 4-*dinitrophenylhydrazone*, m.p. 190—191°). The derived γζ-*diketo*-ζ-m-*anisylheptoic acid*, m.p. 87—88°, and 2% aq. NaOH yield 3-m-*anisyl*-Δ^2-cyclo*pentenone*-2-*acetic acid*, m.p. 100—101°; Ac_2O then affords 3′-*keto*-4-*acetoxy*-7-*methoxy*-1 : 2-cyclo*pentenonaphthalene*, m.p. 177·5—178°, and (probably) some 5-*OMe-isomeride*, m.p. 196·5—198°. Reinvestigation (*loc. cit.*) of the hydrogenation of 4 : 6-dimethoxy-1 : 2-*cyclo*pentadienonaphthalene-3′-acetic acid shows that the acid, $C_{17}H_{22}O_4$, m.p. 117—118°, is a mixture (*A*) of stereoisomerides; the main constituent is 4 : 6-*dimethoxy*-5 : 6 : 7 : 8-*tetrahydro*-1 : 2-cyclo*pentenonaphthalene*-3′-*acetic acid*, m.p. 131—132·5°. With boiling HI (*d* 1·7)–AcOH (30 min.), followed by Me_2SO_4–aq. KOH–MeOH, (*A*) yields 4-*methoxy*-7 : 8-*dihydro*-1 : 2-cyclo*pentenonaphthalene*-3′-*acetic acid*, m.p. 154·5—156·5°, the Me ester of which with Pd–C (N_2) at 300°, followed by hydrolysis, gives (**II**). The non-cryst. acids in the prep. of (*A*) are complex mixtures (deoxygenated) yielding indefinite products on dehydrogenation; their Me esters with Pd–C–N_2 at 220°, followed by hydrolysis, give an *acid*, $C_{15}H_{18}O_2$, m.p. 109·5—111·5°. *o*-Tolyl carbonate (**III**), m.p. 57—57·5°, and (?) $ClCO_2C_6H_4Me$-*o*, b.p. 84°/15 mm. [convertible by C_5H_5N–C_6H_6 into (**III**)], are obtained from *o*-cresol and $COCl_2$–aq. NaOH at 70—75°. With HNO_3 (*d* 1·43) in H_2SO_4 at −15° to 0°, followed by boiling aq. K_2CO_3, (**III**) affords a little 3- + 4-, but mainly 5-nitro-*o*-cresol. 1 : 4 : 2-$C_6H_3MeCl{\cdot}OMe$, obtained from 1 : 4 : 2-$C_6H_4MeCl{\cdot}NH_2$ through the diazo-reaction and subsequent methylation, is converted by AcCl–CS_2–$AlCl_3$ into 6-*chloro*-4-*methoxy*-3-*methylacetophenone*, m.p. 45·5—46°; its *furfurylidene* derivative, m.p. 78—79°, and boiling conc. HCl–EtOH give 2-(4′-*chloro*-6′-*methoxy*-m-*tolyl*)*furan*-5-β-*propionic acid*, m.p. 175—177° (slight sintering) (*Me* ester, m.p. 77—78°) (attempts to open the furan ring failed). 3′-Keto-4 : 6-dimethoxy-1 : 2-*cyclo*pentenonaphthalene and SeO_2–AcOH (b.p.) give 2′ : 3′-*diketo*-4 : 6-*dimethoxy*-1 : 2-cyclo*pentenonaphthalene*, m.p. 243—245° (decomp.) [*quinoxaline* derivative, m.p. 247°, from *o*-$C_6H_4(NH_2)_2$ in AcOH], converted by H_2O_2–aq. NaOH into 2-*carboxy*-4 : 6-*dimethoxy*-1-*naphthylacetic acid*, m.p. 255—257° (decomp.). A. T. P.

Synthesis of substances related to the sterols. XLI. Androstenedione. I. R. H. Martin and (Sir) R. Robinson (*J.C.S.*, 1943, 491—497; cf. A., 1941, II, 295).—A mixture of a max. of eight (probably less) *dl*-stereoisomerides of androstenedione is probably prepared. 2 : 1-$OMe{\cdot}C_{10}H_4{\cdot}CHO$ and H_2–EtOH–Raney Ni at 100°/100 atm. give 6-*methoxy*-5-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (**I**), m.p. 51·5—52° (HI–AcOH give the 6-*OH*-compound, m.p. 113·5—114·5°), better prepared by a similar hydrogenation of 1 : 2-$C_{10}H_6Me{\cdot}OH$, followed by Me_2SO_4–aq. NaOH at 80°, then at 100°. (**I**) and CrO_3–aq. AcOH at <20° yield 1-keto-6-methoxy-5-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene (**II**), m.p. 112—113° (2 : 4-*dinitrophenylhydrazone*, m.p. 249—250°), converted by Et_2O–MgMeI–C_6H_6, followed by S at 215°, into 2-*methoxy*-1 : 5-*dimethylnaphthalene*, m.p. 96—97°; HI–AcOH gives 1 : 5 : 2-$C_{10}H_5Me_2{\cdot}OH$, m.p. 161—162°. $Me_2C_2O_4$–dry NaOMe–C_6H_6 (under N_2) and (**II**)–C_6H_6 at room temp., then at b.p., afford *Me* 1-*keto*-6-*methoxy*-5-*methyl*-1 : 2 : 3 : 4-*tetrahydro*-2-*naphthylglyoxylate*, m.p. 136—137°, which loses CO at 170—180° to give *Me* 1-*keto*-6-*methoxy*-5-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-2-*carboxylate* (**III**), m.p. 100—101° (immersed at 93°) (2 : 4-*dinitrophenylhydrazone*, m.p. 223—224° after darkening at 195°). (**III**) and boiling MeI–NaOMe–C_6H_6 give the 2-*Me* derivative, m.p. 89—90·5°, which with $CH_2Br{\cdot}CO_2Me$–Zn–C_6H_6–Et_2O (+ I) at 70° yields (chromatographic separation) *Me* 1-*hydroxy*-6-*methoxy*-2-*carbomethoxy*-2 : 5-*dimethyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*naphthylacetate* (**IV**), m.p. 106·5—108°; $SOCl_2$–C_6H_6–C_5H_5N at room temp., followed by boiling aq. KOH–MeOH, gives a mixture of the cis-*anhydride* (**V**), m.p. 204—205°, of 1-*carboxymethylene*-6-*methoxy*-2 : 5-*dimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-2-*carboxylic acid*, and the *trans*-1 : 2-dicarboxylic acid [in one experiment, 1-*keto*-6-*methoxy*-2 : 5-*dimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 113—114° (2 : 4-*dinitrophenylhydrazone*, m.p. 229°), was also isolated]. (**IV**) and HCl–C_6H_6–$CaCl_2$ at room temp. give stereoisomeric *Me*$_2$ esters (**VI**), $C_{18}H_{22}O_5$, b.p. 150°/0·05 mm. and m.p. 105·5—106·5°. (**V**) (crude) is hydrolysed by KOH–EtOH, and the resulting K salts reduced by 2% Na–Hg to the H_2-acids, and esterified (CH_2N_2) to the α-*Me*$_2$ ester (**VII**), m.p. 112—113°, of 2-*carboxy*-6-*methoxy*-2 : 5-*dimethyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*naphthylacetic acid*; the β-*Me*$_2$ ester, m.p. 53—54°, also formed is obtained

cryst. through the *β-Me H* ester (**VIII**), m.p. 149—150°, and CH_2N_2. The *α-Me H* ester (**IX**) has m.p. 137—139°. A mixture of *α-* (main product) and *β-Me*$_2$ esters is obtained by catalytic reduction of (**VI**), using PtO_2 in AcOH or EtOAc, Pd–C or Pd-black in $COMe_2$, or $SrCO_3$–Pd, or Raney Ni at 60°/25 atm. Boiling KOH–MeOH converts the Me$_2$ esters into the *α-*, m.p. 217—217·5° (slight sintering), and *β-dicarboxylic acid*, m.p. 198—200°, and thence (Ac_2O) the *α-*, m.p. 173—174°, and *β-anhydride*, m.p. 168—169°, respectively. Thermodynamic dissociation consts. of the dicarboxylic acids are investigated [by J. C. Speakman], but spatial structure could not be proved. It is probable that CO_2Me and $CH_2{\cdot}CO_2Me$ are *cis-* in the *α-* and *trans-* in the *β-*series. Reduction of (**VI**) using Raney Ni (above) is unreliable, and in one experiment, much degradation occurred; after hydrolysis with KOH–EtOH, followed by Ac_2O, (**V**) was isolated; also formed were 1 : 2 : 5 : 6-$C_{10}H_4Me_3{\cdot}OMe$ and (?) 6-*methoxy*-2 : 5-*dimethyl*-3 : 4-*dihydro*-1-*naphthylacetic acid*, m.p. 180—192° (H_2–Pd–$SrCO_3$–EtOAc–$COMe_2$ gives the *H*$_4$-*acid*, m.p. 155·5—159°). (**VII**) with HI (*d* 1·7)–AcOH followed by boiling H_2SO_4–MeOH gives *Me α-2-carboxy-6-hydroxy-2 : 5-dimethyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*naphthylacetate*, m.p. 169—170° (+ MeOH), and *α-2-carbomethoxy-6-hydroxy-2 : 5-dimethyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*naphthylacetic acid*, m.p. 179·5—180·5°. When the crude demethylation product of (**VII**) or the corresponding dicarboxylic acid is refluxed with MeOH–H_2SO_4, the *Me*$_2$ ester (**X**), m.p. 122—123°, of the phenoldicarboxylic acid is obtained; the *β-*dicarboxylic acid is demethylated and esterified (HCl–MeOH) to give the *Me*$_2$ ester, m.p. 125—126°, isomeric with (**X**). (**X**) and H_2–dry dioxan–Raney Ni give only a trace of *Me 2-carbomethoxy-6-hydroxy-2 : 5-dimethyldecahydro-2-naphthylacetate*, b.p. 180° (bath)/0·05 mm.; there is considerable deoxygenation. The chloride from (**IX**) and $SOCl_2$–Et_2O (+ C_5H_5N) with Et_2O–CH_2N_2 in C_6H_6 gives the diazo-ketone, which with Ag_2O–MeOH affords *Me α-2-carbomethoxy-6-methoxy-2 : 5-dimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-1-*β-propionate*, m.p. 84—85°; NaOMe–C_6H_6 (under N_2) then gives *Me 3′-keto-6-methoxy-2 : 5-dimethyl*-1 : 2 : 3 : 4-*tetrahydro*-1 : 2-cyclo*pentenonaphthalene*-2′-*carboxylate*, m.p. 107·5—108·5°, converted by boiling HI–AcOH into 6-*hydroxy-3′-keto-2 : 5-dimethyl*-1 : 2 : 3 : 4-*tetrahydro*-1 : 2-cyclo*pentenonaphthalene*-α (**XI**), m.p. 189—191° (vac.). (**VIII**) similarly yields the *OH-ketone-β*, m.p. 230—231° (vac.). The use of 2% Pd–$SrCO_3$ as catalyst for hydrogenations in dioxan is illustrated. Thus PhOH at 20°/113 atm., then 75—140°/125 atm., gives almost quant. yield of *cyclo*hexanol, *p*-$C_6H_4(OMe)_2$ affords 1 : 4-dimethoxy*cyclo*hexane, *p*-OH·$C_6H_4{\cdot}CO_2Et$ in pure dioxan at 15°/118 mm., then 155°/150 atm. and 157°/90 atm., or in EtOAc at 140—150°/140 atm., yields *trans*-4-carbethoxy*cyclo*hexanol. (**X**) is not similarly reduced, but (**XI**) (in dioxan) at 196°/134 atm., then 202°/133 atm., gives stereoisomeric 6 : 3′-*dihydroxy*-2 : 5-*dimethyldecahydro*cyclo*pentenonaphthalenes*, a colourless glass, oxidised by CrO_3–AcOH at 10—15° to a mixture of diketones containing 6 : 3′-*diketo*-2 : 5-*dimethyldecahydro*-1 : 2-cyclo*pentenonaphthalene*-x-α, m.p. 116—117°. The mixed diketones (not cryst.) with $NaNH_2$ in boiling Et_2O (N_2) for 6 hr., followed by COMe·$[CH_2]_2{\cdot}$NMeEt,I in EtOH (N_2), give mixed (?) *androstenediones* (absorption in EtOH confirms C:C·CO).

A. T. P.

Crystalline bisulphite additive compounds of menadione [2-methyl-1 : 4-naphthaquinone]. F. Ablondi, R. W. Price, B. R. Baker, and G. H. Carlson (*J. Amer. Chem. Soc.*, 1943, **65**, 1776).—Cryst. *LiHSO*$_3$, *NH*$_4$*HSO*$_3$, and *Ca*$(HSO_3)_2$, m.p. (air-dried) 97—98°, (anhyd.) 115—117° (decomp.), derivatives of 1 : 2 : 4-O:C$_6$H·Me:O are prepared.

R. S. C.

Synthesis of 2-methyl-1 : 4-naphthaquinone-8-sulphonic acid. A. Bendich and E. Chargaff (*J. Amer. Chem. Soc.*, 1943, **65**, 1568—1569).—2-$C_{10}H_7Me$ and $ClSO_3H$ in CCl_4 at −10° to room temp. give 2 : 8- (49% isolated as Ba salt) and 2 : 1-$C_{10}H_4Me{\cdot}SO_3H$ (cf. Vesely *et al.*, A., 1930, 1173). 2 : 8-$C_{10}H_6Me{\cdot}SO_3K$ and PCl_5 at 100° give the sulphonyl chloride, m.p. 94—95°, and thence (conc. aq. NH_3) the sulphonamide, m.p. 197°, which with CrO_3–AcOH at 80°—the b.p. gives 2-*methyl*-1 : 4-*naphthaquinone*-8-*sulphonamide*, m.p. 231—232° (decomp.). $NaNO_2$–H_2SO_4–AcOH then gives 2-methyl-1 : 4-naphthaquinone-8-sulphonic acid [*Ba*, *K*, and *Tl*, m.p. 263—264° (decomp.), salts], which has little or no vitamin-*K* activity.

R. S. C.

Synthesis of the pentacene ring system. C. F. H. Allen and J. W. Gates, jun. (*J. Amer. Chem. Soc.*, 1943, **65**, 1502—1503).—1 : 3-Diphenylisobenzfuran and *p*-O:C_6H_4:O in boiling EtOH give 7 : 12 : 5 : 14-*diepoxy*-5 : 7 : 12 : 14-*tetraphenyl*-5 : 5a : 6a : 7 : 12 : 12a : 13a : 14-*octahydropentacene*-6 : 13-*quinone*, m.p. 197—198°, converted by conc. H_2SO_4 at −10° into 5 : 7 : 12 : 14-tetraphenylpentacene-6 : 13-quinone (A., 1942, II, 320).

7 : 12 : 5 : 14-*Diepoxy*-5 : 7 : 12 : 14-*tetraphenyl*-2 : 3 : 9 : 10-*tetramethyl*-5 : 5a : 6a : 7 : 12 : 12a : 13a : 14-*octahydropentacene*-6 : 13-*quinone* is similarly prepared.

R. S. C.

IV.—STEROLS AND STEROID SAPOGENINS.

17-Amino-10 : 13-dimethyl*cyclo*pentanopolyhydrophenanthrene compounds —See B., 1943, III, 303.

Steroids with ethylenic linkings between quaternary carbon atoms. III Structure of α-spinasterol. H. E. Stavely and G. N. Bollenback (*J. Amer. Chem. Soc.*, 1943, **65**, 1600—1603; cf. A., 1943, II, 332).—γ-Cholestenyl acetate (**I**) is unchanged by PtO_2, Pt- or Pd-black unless the catalyst has been treated with H_2 (cf. Wieland *et al.*, A., 1943, II, 268). In presence of H_2 all three catalysts isomerise (**I**). When Pd-black is first shaken in EtOAc with H_2, it then isomerises (**I**) under N_2, but this treatment fails with PtO_2 or Pt-black. α-Spinasterol is proved to be the $\Delta^{8(9)}$-compound. Its acetate with CrO_3–AcOH at room temp. gives a mixture (cf. Simpson, A., 1937, II, 339), resolved by chromatography into 8 : 9- (**II**), m.p. 229—230°, $[\alpha]_D$ −32±1·5°, and 8 : 14-*epoxy*-3-*acetoxy*-Δ^{---}-*stigmasten*-7-*one* (**III**), m.p. 171—173°, $[\alpha]_D^{24}$ −77±3°, both having no selective adsorption at >230 mμ., and a residue which by hydrolysis (HCl–EtOH), treatment with Girard's reagent *T*, acetylation, and chromatography yields 3-*acetoxy*-$\Delta^{8(9):\,?-(23)}$-*stigmastadien*-7-*one* (3%), m.p. 202—204°, $[\alpha]^{23}$ −36±2° (absorption max. at 252 mμ., ε 8300), 3-*acetoxy*-$\Delta^{8(11):\,8(14)\,.\,?(23)}$-*stigmastatrien*-3-*one*, m.p. 190—192°, $[\alpha]_D^{3}$ −24±2° [absorption max. at 299 mμ., ε 5300; also obtained from (**II**) or (**III**) by HCl–EtOH and then Ac_2O–C_5H_5N], and 3-*acetoxy*-$\Delta^{8(14)}$-*stigmasten*-7-*one*, m.p. 140—141°, $[\alpha]_D$ −53±1·5° (absorption max. at 260 mμ., ε 7800; reduced by H_2–Pd-black or –PtO_2 in AcOH to *α-spinastenyl acetate*, m.p. 117°, $[\alpha]_D$ +13±1°). [α] are in $CHCl_3$.

R. S. C.

Preparation and properties of the 7-epimeric cholestane-3(β) : 7-diols. O. Wintersteiner and (Miss) M. Moore (*J. Amer. Chem. Soc.*, 1943, **65**, 1503—1507).—H_2–PtO_2 converts 7-ketocholesteryl acetate (**I**) in AcOH into 3(β)-*acetoxycholestan*-7(α)- (**II**), m.p. 71—75°, $[\alpha]_D^{23}$ +35·3°, and -7(β)-*ol* (**III**), *forms*, m.p. 116—117° and 124°, $[\alpha]_D^{23}$ 0, with small amounts of β-cholestanyl acetate and 7-ketocholestanyl acetate (**IV**), m.p. 149—149·5°, $[\alpha]_D^{2}$ −36·0° (cf. Marker *et al.*, A., 1940, II, 17); with H_2–PtO_2 in EtOAc, (**I**) gives (**IV**), which in AcOH yields only (**II**) and (**III**). CrO_3 oxidises (**II**) or (**III**) to (**IV**). Boiling 5% KOH–MeOH hydrolyses (**II**) and (**III**) to *cholestane*-3(β) : 7(α)- (**V**), *forms*, m.p. 156—158° and 167—168°, $[\alpha]_D^{24}$ +52·9° {*diacetate* [prep. from (**II**)], *forms*, m.p. 64—69°, 74—78°, and 81—87°, $[\alpha]_D^{24}$ +54·7°; *dibenzoate*, m.p. 151—152°, $[\alpha]_D^{23}$ +67·6°}, and -3(β) : 7(β)-*diol*, m.p. 152—153°, $[\alpha]_D$ +8·1° (*diacetate*, m.p. 138—139°, $[\alpha]_D$ −17·2°; *dibenzoate*, m.p. 153—154°, $[\alpha]_D^{24}$ +23·0°), respectively. In C_5H_5N at room temp., (**II**) gives 7(α)-*p-toluenesulphonyloxy*-3(β)-*acetoxycholestane*, m.p. 152·5—153°, $[\alpha]_D^{24}$ +11·6°. With PCl_5–$CaCO_3$–$CHCl_3$ at 0°, (**II**) gives 3(β)-*acetoxy*-7-*cholestanyl chloride*, m.p. 118—119°, $[\alpha]_D^{23}$ −21·7°, and thence (20% KOH–MeOH) 7-*chlorocholestan*-3(β)-*ol*, m.p. 170·5—171·5°, $[\alpha]_D^{23}$ −19·8°; Walden inversion may have occurred. With $SOCl_2$–$CaCO_3$–Et_2O, (**II**) gives *di*-3(β)-*acetoxy*-7(α)-*cholestanyl sulphite*, m.p. 131·5—133·5°, hydrolysed by 5% KOH–MeOH to (**V**). [α] are in $CHCl_3$.

R. S. C.

Dehydration of the 7-epimeric 3(β)-acetoxycholestan-7-ols. Transformation products of γ-cholestenol. O. Wintersteiner and (Miss) M. Moore (*J. Amer. Chem. Soc.*, 1943, **65**, 1507—1513).—Dehydration of 3(β)-acetoxycholestan-7(β)-ol by $CuSO_4$ in boiling xylene, *p*-$C_6H_4Me{\cdot}SO_2Cl$ in boiling C_5H_5N, or PCl_5 in $CHCl_3$ at 0°, by elimination of $ArSO_3H$ from the 7-*p*-toluenesulphonate by NaI and C_5H_5N, or of HCl from the 7(α)-chloride by KOAc–AcOH at 130° gives an inseparable mixture (*A*), containing mostly γ- (Δ$^{7(8)}$-)cholestenyl acetate. Pd–H_2 isomerises (*A*) in AcOH to give a good yield of α-(Δ$^{8(14)}$-)cholestenyl acetate. With OsO_4 in Et_2O at room temp. (6 days) and then Na_2SO_3 in hot aq. EtOH and acetylation, (*A*) gives 3(β) : 7-*diacetoxycholestan*-8-*ol*, m.p. 168—169°, $[\alpha]_D$ −39·8°, and thence by hot 5% KOH–MeOH *cholestane*-3(β) : 7 : 8-*triol*, m.p. 176—178°, $[\alpha]_D^{1}$ −12·9° (no digitonide). (*A*) consumes 2 BzO_2H in $CHCl_3$ in 8 days (cf. Schenck *et al.*, A., 1937, II, 59), giving 8 : 14-*epoxy*-3(β)-*acetoxycholestan*-7-*ol* (**I**), m.p. 122—123°, $[\alpha]_D^{3}$ +6·1°, converted by Ac_2O–C_5H_5N at room temp. into the 3(β) : 7-*diacetate* (**II**), m.p. 162—163°, $[\alpha]^{23}$ −11·9°. 5% hot KOH–MeOH hydrolyses (**I**) or (**II**) to 8 : 14-*epoxycholestane*-3(β) : 7-*diol*, m.p. 186—187°, $[\alpha]_D^{1}$ +81° (digitonide, decomp. 225°). Some samples of (*A*) give, besides (**I**), an *isomeride* thereof, m.p. 145·5—146°, $[\alpha]_D^{23}$ +27·6° (derived *diacetate*, sinters 59°, m.p. 63—64°). CrO_3–AcOH at room temp. converts (**I**) into 8 : 14-*epoxy*-3(β)-*acetoxycholestan*-7-*one* (**III**), m.p. 139·5—140°, $[\alpha]_D$ −75·7° (slight absorption at <240 mμ.; no semicarbazone), converted by conc. HCl in boiling EtOH into 3(β)-*acetoxy*-Δ$^{8(9):\,14(15)}$- or -Δ$^{9(11)\cdot\,8(14)}$-*cholestadien*-7-*one*, sinters 163°, m.p. 166°, $[\alpha]_D^{21}$ −17·6° [absorption max. at 297 (ε 4800), min. at 257 (ε 1500), end at <240 mμ. in EtOH; 2 : 4-*dinitrophenylhydrazone*, m.p. 225—228°, obtained also from (**III**)]. This is reduced by H_2–Pd in EtOH to 3(β)-*acetoxy*-Δ$^{8(14)}$-*cholesten*-7-*one*, m.p. 141·5—142·5°, $[\alpha]_D^{21}$ −62·2° [absorption max. at 262·5 mμ. (ε 9500); 2 : 4-dinitrophenylhydrazone, m.p. 210—211°], further reduced in AcOH to α-cholestenyl + 7-ketocholestanyl acetates. [α] are in $CHCl_3$.

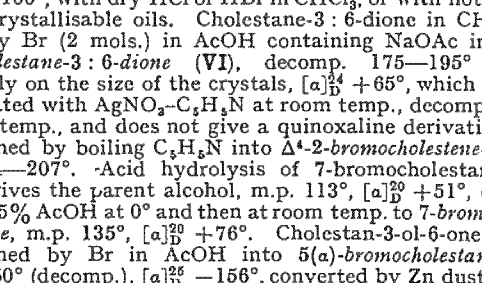
R. S. C.

Oxidation products of α-cholestenyl acetate. O. Wintersteiner and (Miss) M. Moore (*J. Amer. Chem. Soc.*, 1943, **65**, 1513—1516).—Neutral products obtained from α-cholestenyl acetate (**I**) by CrO_3–AcOH–C_6H_6 give, by chromatography, 8 : 14-epoxy-3(β)-acetoxycholestan-7-one with smaller amounts of 3(β)-*acetoxy*-Δ$^{8(14)}$-*chole-*

sten-15-*one*, m.p. 134—135°, $[\alpha]_D$ −118° [absorption max. at 259 mμ. (ε 12,750) in EtOH; 2 : 4-*dinitrophenylhydrazone*, m.p. 208—209°; derived 3-*OH-ketone*, m.p. 145—146° (digitonide); slowly hydrogenated to (**I**)], 8 : 14-*epoxy*-3(β)-*acetoxycholestan*-15-*one*, m.p. 180—181°, $[\alpha]_D^{22}$ +4·7° (in conc. HCl–EtOH gives mixed dienones), (?)8 : 14-*dihydroxy*-3(β)-*acetoxycholestane*-7 : 15-*dione*, m.p. 184—185°, $[\alpha]_D^{22}$ +73·5°, and (?)14-*hydroxy*-3(β)-*acetoxy*-$\Delta^{8(9)}$-*cholestene*-7 : 15-*dione*, m.p. 218—219° (decomp.), $[\alpha]_D^1$ +143·5° [absorption max. at 254 mμ. (ε 10,400)]. [α] are in $CHCl_3$. R. S. C.

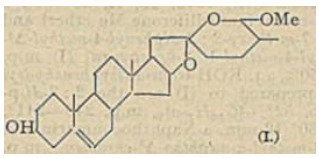
Bromination of steroid ketones. L. H. Sarett, P. N. Chakravorty, and E. S. Wallis (*J. Org. Chem.*, 1943, **8**, 405—416).—Cholestane-3 : 6-dione is converted by Br (9 mols.) in dry $CHCl_3$–AcOH into Δ^4-2 : 4 : 7 : 7-*tetrabromocholestene*-3 : 6-*dione* (**I**), m.p. 190°, $[\alpha]_D^{20}$ +22°, converted by 15% HBr–AcOH in $CHCl_3$ into Δ^4-4 : 7 : 7-tribromocholestene-3 : 6-dione (**II**), m.p. 195°, $[\alpha]_D^0$ +16°, also obtained if the prep. of (**I**) is prolonged or if (**I**) in AcOH–$CHCl_3$ is treated with Br + I. (**I**) in boiling C_6H_6 containing a little EtOH is reduced by fine Fe powder to Δ^4-4 : 7-dibromocholestene-3 : 6-dione (**III**), m.p. 175°, $[\alpha]_D^{20}$ +82°, whereas Fe and boiling EtOH reduce (**I**) to cholestane-3 : 6-dione, m.p. 171°. Fe powder in boiling C_6H_6 containing EtOH reduces (**I**), (**II**), or (**III**) to Δ^4-4-bromocholestene-3 : 6-dione, m.p. 169·5°, $[\alpha]_D^{20}$ −38°, the constitution of which follows from its conversion by *o*-$C_6H_4(NH_2)_2$ into the same *quinoxaline* derivative, $C_{33}H_{46}ON_2$, m.p. 143° (opaque; clear at 157°), as is obtained from cholestane-3 : 4 : 6-trione. (**I**) is converted by $AgNO_3$ in C_5H_5N at room temp. into $\Delta^{4:7}$-2 : 4 : 7-*tribromocholestadiene*-3 : 6-*dione*, m.p. 164°, $[\alpha]_D^{20}$ −38°, transformed by HBr–AcOH–$CHCl_3$ into $\Delta^{4:7}$-4 : 7-dibromocholestadiene-3 : 6-dione, m.p. 182°, $[\alpha]_D^{20}$ −18°, and by Fe powder in boiling C_6H_6–EtOH into $\Delta^{4:7}$-7-bromocholestadiene-3 : 6-dione, m.p. 182°, $[\alpha]_D^0$ −141°. Attempted hydrolysis of 5(α) : 7-dibromocholestan-3-ol-6-one acetate gives only intractable gels whereas acid hydrolysis of the corresponding 5(β)-derivative leads smoothly to 5(β) : 7-dibromocholestan-3-ol-6-one, decomp. 117—119°, $[\alpha]_D^0$ −50°, re-acetylated by boiling Ac_2O to the parent acetate and oxidised by CrO_3 in AcOH to 5(β) : 7-*dibromocholestane*-3 : 6-*dione*, decomp. 100°, $[\alpha]_D^{20}$ −41°, which is converted by KOAc and boiling aq. AcOH into Δ^4-7-bromocholestene-3 : 6-dione (**IV**), m.p. 130—131°, $[\alpha]_D^{20}$ −41°. (**IV**) is reduced by Zn dust in boiling EtOH to cholestane-3 : 6-dione, and converted by Br in $CHCl_3$–AcOH containing NaOAc into Δ^4-2 : 7-*dibromocholestene*-3 : 6-*dione* (**V**), m.p. 119°, $[\alpha]_D^{20}$ +118° (whence a *diquinoxaline* derivative, $C_{39}H_{46}N_4$, m.p. 194°). Further bromination of (**V**) proceeds very slowly and only initial material is isolated from the product. Cholestane-3(β) : 5(α)-diol-6-one in $CHCl_3$ is converted by Br (1 mol.) in AcOH at 35° into 7-*bromocholestane*-3(β) : 5(α)-*diol*-6-*one*, decomp. 250°, $[\alpha]_D^{26}$ −24° [*acetate* (+ 1MeOH), m.p. 172°], oxidised by CrO_3 in 90% AcOH to 7-bromocholestan-5(α)-ol-3 : 6-dione, m.p. 165—171°, which is reduced by Zn dust and boiling EtOH to cholestan-5(α)-ol-3 : 6-dione, m.p. 232°; attempted dehydration with 95% HCO_2H at room temp. or 100°, with dry HCl or HBr in $CHCl_3$, or with hot Ac_2O gives only uncrystallisable oils. Cholestane-3 : 6-dione in $CHCl_3$ is converted by Br (2 mols.) in AcOH containing NaOAc into 2 : 2-*dibromocholestane*-3 : 6-*dione* (**VI**), decomp. 175—195° depending principally on the size of the crystals, $[\alpha]_D^{24}$ +65°, which gives an oil when heated with $AgNO_3$–C_5H_5N at room temp., decomposes slowly at room temp., and does not give a quinoxaline derivative. (**VI**) is transformed by boiling C_5H_5N into Δ^4-2-*bromocholestene*-3 : 6-*dione*, m.p. 204—207°. Acid hydrolysis of 7-bromocholestan-3-ol-6-one acetate gives the parent alcohol, m.p. 113°, $[\alpha]_D^{20}$ +51°, oxidised by CrO_3 in 95% AcOH at 0° and then at room temp. to 7-*bromocholestane*-3 : 6-*dione*, m.p. 135°, $[\alpha]_D^{20}$ +76°. Cholestan-3-ol-6-one in Et_2O is transformed by Br in AcOH into 5(α)-*bromocholestan*-3-*ol*-6-*one*, m.p. ~150° (decomp.), $[\alpha]_D^{25}$ −156°, converted by Zn dust and EtOH into the parent compound and by Ac_2O into the acetate, m.p. 164°; it is oxidised to 5(α)-*bromocholestane*-3 : 6-*dione*, decomp. 80—85°, $[\alpha]_D^{26}$ +140°, which slowly decomposes with loss of HBr at room temp. and is rapidly transformed by boiling C_5H_5N into Δ^4-cholestene-3 : 6-dione. $[\alpha]_D$ are in $CHCl_3$. H. W.

Sterols. CLIX. Sapogenins. LXXI. Bethogenin. R. E. Marker, R. B. Wagner, C. H. Ruof, P. R. Ulshafer, D. P. J. Goldsmith (*J. Amer. Chem. Soc.*, 1943, **65**, 1658—1659).—Bethogenin (**I**) (Noller *et al.*, A., 1943, II, 333) is an artefact in *Beth* root, being obtained from kryptogenin (**II**) by treating with HCl–MeOH and



then 2% KOH–MeOH. It has the structure shown. With HBr–AcOH it regenerates (**II**) or a similar diketone with hydrolysis of the OMe and with NH_2OH in C_5H_5N gives the dioxime of (**II**). R. S. C.

Saponins and sapogenins. XXIII. Constitution of bethogenin. C. R. Noller and M. R. Barusch (*J. Amer. Chem. Soc.*, 1943, **65**, 1786).—The structure below is suggested for bethogenin (**I**). (**I**) or its acetate with HBr–AcOH loses OMe and gives a *diacetate*, $C_{31}H_{46}O_6$, m.p. 148—149°, $[\alpha]_D^{26}$ −161° in dioxan (*dioxime*, m.p. 194—195°), hydrogenated (PtO_2; EtOH) to a *H_2-diacetate*, m.p. 116—117°, $[\alpha]_D$ −11° in dioxan [CO proved by absorption spectrum; saturated towards $C(NO_2)_4$].



H_2–PtO_2 reduces (**I**) in EtOH, with removal of OMe, to an unsaturated ketone (*diacetate*, $C_{31}H_{46}O_6$, m.p. 142—144°, $[\alpha]_D^{24}$ −156° in dioxan), and, by exhaustive treatment, a saturated, non-ketonic *substance*, $C_{27}H_{46}O_4$, m.p. 203—208·6°, $[\alpha]_D^{25}$ −57·7° in dioxan, converted by Ac_2O–C_5H_5N into an *acetate*, $C_{29}H_{46}O_4$, m.p. 204—207·5°, $[\alpha]_D^{25}$ −62·2° in dioxan. Kryptogenin may be a keto-aldehyde, since with HBr–AcOH, (**I**) but not diosgenin, tigogenoic or chlorogenoic acid, or Me chlorogenoate, yields a substance which gives a pink colour with Schiff's reagent and a red colour with 1 : 4-$C_{10}H_6(OH)_2$–HCl–AcOH. R. S. C.

V.—TERPENES AND TRITERPENOID SAPOGENINS.

Triterpene group. X. Continuation of parts II and V. J. C. E. Simpson and R. A. Morton (*J.C.S.*, 1943, 477—486; cf. A., 1938, II, 448; 1939, II, 331).—The previous hypothesis of the presence of an aromatic ring in the hydroxydione, $C_{30}H_{44}O_3$ (obtained originally from β-amyrin by mild S-dehydrogenation and subsequent oxidation), and its congeners is withdrawn, and the results obtained by a study of these compounds are critically considered with reference to recent publications of Ruzicka *et al.* (A., 1942, II, 371) and Kon *et al.* (*ibid.*, 148). It is concluded that neither the Ruzicka nor the Kon formulation for the compound accounts for the properties of certain derivatives of this substance, and this is attributed to incorrect siting of the chromophore. The substances discussed have been examined both chemically and spectrographically, and NO_2-derivatives of the cholesterol series have been included. Generalisations are made respecting the scope and limitation of the Liebermann–Burchard and the $C(NO_2)_4$ reaction for the diagnosis of unsaturation in polycyclic hydroaromatic compounds. Reduction (Na–C_5H_{11}·OH) of the OAc-compound (**I**), $C_{32}H_{46}O_5$, gives an acid (**II**), $C_{30}H_{46}O_4$, m.p. 264·5—266·5° [*Ac_2 Me ester* (**III**), $C_{35}H_{46}O_8$, m.p. 228—229°, $[\alpha]_D$ +63° in $CHCl_3$], and a neutral fraction, which after acetylation yields a *substance*, $C_{30}H_{48}O_3$, m.p. 195—205°, clear at ~250°. Oxidation of (**III**) by BzO_2H affords an *oxide*, $C_{35}H_{56}O_7$, m.p. 233·5—234·5°. Acetylation (Ac_2O–C_5H_5N) of (**II**) leads to the *Ac_2-acid*, m.p. 249—251°, $[\alpha]^{19}$ +59° in $CHCl_3$, which is oxidised (CrO_3–AcOH) to an *acid*, $C_{34}H_{52}O_7$, m.p. 285—286°, esterified (CH_2N_2) to the *Ac_2 Me keto-dihydro-ester*, $C_{35}H_{54}O_7$, m.p. 275—277°, also obtained by oxidation (CrO_3) of (**III**). Oxidation (CrO_3) of (**II**) gives a *diketo-acid*, $C_{30}H_{46}O_4$, m.p. 192—194°. Reduction of (**I**) with 2½% C_5H_{11}·ONa–C_5H_{11}·OH affords an *acid*, $C_{30}H_{46}O_5$, m.p. 240—241° (decomp. on keeping), which is esterified (CH_2N_2) and acetylated to the *Ac Me ester*, $C_{33}H_{50}O_8$, m.p. 179—180·5° (decomp. on keeping). PCl_5 and the OH-compound (**IV**), $C_{30}H_{44}O_4$, yield a *substance*, $C_{30}H_{42}O_3$, m.p. 295—297° (decomp.). The lactone obtained in small yield from the oxidation products of (**IV**) is reduced (2½% C_5H_{11}·ONa) to an *acid*, $C_{28}H_{40}O_5$, m.p. 251—253° which is esterified to the Me ester, also obtained by hydrolysis of the lactone. F. R. S.

Sapogenins.—See B., 1943, III, 280.

VI.—HETEROCYCLIC.

Rubber, polyisoprenes, and allied compounds. V. Chemical linking of rubber and of other olefines with phenol–formaldehyde resins. J. I. Cunneen, E. H. Farmer, and H. P. Koch (*J.C.S.*, 1943, 472—476).—1-Methyl*cyclo*hexene (**I**) in excess with saligenin (**II**) at 180° in sealed tubes gives 12-*methyl*-1 : 2 : 3 : 4 : 12 : 13-*hexahydroxanthen*, b.p. 138—139°/10 mm., with a little o-o-*hydroxybenzyl*-12-*methyl*-1 : 2 : 3 : 4 : 12 : 13-*hexahydroxanthen*. Dihydromyrcene with (**II**) similarly affords *mono*-, b.p. 118°/0·05 mm. [mainly 2 : 2-*dimethyl*-3-(γ-*methyl*-Δ^γ-*pentenyl*)*chroman*], and *di-saligeninodihydromyrcene*, b.p. 200—205°/0·05 mm. [mainly α-(2 : 2-*dimethylchromanyl*-3)-β-(2 : 3-*dimethylchromanyl*-2)-*ethane*]. When purified rubber (1 mol.) in C_6H_6 is heated with (**II**) in two different proportions (0·18 and 0·27 mol.) two distinct oxygenated products are formed, containing hydroxylic (presumably phenolic) as well as ethereal O, in the ratios 1 : 2 and 5 : 8, so indicating that most of the O is present in simple chroman units. Sepctrographic measurements confirm the constitutions assigned, and 7 : 12-*dimethyl*-1 : 2 : 3 : 4 : 12 : 13-*hexahydroxanthen*, b.p. 147—150°/10 mm., from (**I**) and 2 : 5 : 1-OH·C_6H_3Me·CH_2·OH, has been prepared for comparison. The relation of chroman-formation to the formation of PhOH–CH_2O resins is discussed and it is suggested that rubber, isoprenic olefines, and doubtless most olefinic substances combine by virtue of their

unsaturation with the condensation products of PhOH and CH_2O to give chroman derivatives. F. R. S.

Action of Grignard reagents on benzpyrones. I. Preparation of some chromens from 4-substituted coumarins. A. R. S. Kartha and K. N. Menon (*Proc. Indian Acad. Sci.*, 1943, **18**, **A**, 28—30).—7-Methoxy-4-methylcoumarin (4-methylumbelliferone Me ether) and boiling MgPhBr–C_6H_6 give *7-methoxy-2 : 2-diphenyl-4-methyl-*Δ^3*-chromen* [*7-methoxy-2 : 2-diphenyl-4-methyl-1 : 2-benzpyran*] (**I**), m.p. 60—65°, hydrolysed by boiling 50% aq. KOH to *m-anisyl benzhydryl ether*, m.p. 105·5°. Similarly prepared to (**I**) are the *2 : 2-di-p-anisyl*, m.p. 110°, *-dibenzyl*, m.p. 52°, *-*($C_{10}H_7$-α)$_2$, m.p. 240—241°, and *-Me*$_2$ analogue, b.p. 158—160°/12 mm. α-Naphthocoumarin and MgPhBr give *2 : 2-diphenyl-4-methyl-α-naphtho-*Δ^3*-chromen*, m.p. 126—127°. A. T. P.

Tetrahydrobenzpyrans.—See A., 1943, II, 342.

Geometrical isomerism of cyclic acetal derivatives from polyhydric nitro-alcohols. M. Senkus (*J. Amer. Chem. Soc.*, 1943, **65**, 1656).—5-Nitro-2-phenyl-5-methyl-1 : 3-dioxan, m.p. 118·3°, obtained from NO_2·CMe(CH_2·OH)$_2$ and PhCHO (A., 1942, II, 111), is accompanied by a *stereoisomeride*, m.p. 78·4°; these are reduced to *amines*, m.p. 84·0° and 48·2°, respectively. NO_2·CEt(CH_2·OH)$_2$ and PrCHO give similarly *5-nitro-, forms*, b.p. 104—106°/5 mm. and 136·0—136·5°/5 mm., reduced to *5-amino-5-ethyl-2-propyl-1 : 3-dioxan, forms*, b.p. 94—95°/10 mm. and 95°/10 mm., respectively. R. S. C.

Vat dyes.—See B., 1943, II, 344.

Preparation of iodine-containing *X*-ray contrast substances. I. 3 : 5-di-iodo-4-pyridone-*N*-acetic acid ("perabrodil"). W. Baker and A. S. Briggs (*J.S.C.I.*, 1943, **63**, 189—191).—C_5H_5N (100 g.), treated with $AlCl_3$ 2 g., $C_2H_2Cl_4$ 100 g., and Br 1 mol. for 48 hr. at 20—25°, gives 4-pyridylpyridinium bromide hydrobromide, the aq. solution of which, after distilling off $C_2H_2Cl_4$, is heated in an autoclave at 150° for 8 hr., made alkaline, and distilled, leaving a solution of 4-pyridone. This solution is boiled with I and made alternately acid and alkaline 6 times during 1 hr., giving 3 : 5-di-iodo-4-pyridone. This is finally pptd. by acid, and heated with aq. NaOH and CH_2Cl·CO_2H, giving 3 : 5-di-iodo-4-pyridone-*N*-acetic acid, m.p. ~247° (decomp.) (lit. 246°); yield 107 g. S. A. M.

Indole synthesis from a *m*-carboxyphenylhydrazone. C. F. Koelsch (*J. Org. Chem.*, 1943, **8**, 295—299).—*m*-NH_2·C_6H_4·CO_2H, prepared from the NO_2-acid by $(NH_4)_2S$, is best isolated as hydrochloride (**I**). *m*-CO_2H·C_6H_4·N_2Cl and Et *cyclo*pentanone-2-carboxylate (**II**) in aq. NaOH give a (?) formazyl compound. Treating (**I**) in HCl at 0° with, successively, $NaNO_2$, NaOAc, and (**II**) gives Et 2-*m*-carboxybenzeneazo*cyclo*pentanone-2-carboxylate, sinters 105°, m.p. 118—120° (decomp.), converted by boiling 7% Na_2CO_3 (2 min.) into the *hydrazone*, *m*-CO_2H·C_6H_4·NH·N:C(CO_2Et)·[CH_2]$_3$·CO_2H (<70%), m.p. 165—167°. In boiling 10% NaOH this gives *α-ketoadipic acid* m-*carboxyphenylhydrazone*, m.p. 215—218° (gas), and in boiling 1 : 10 (vol.) H_2SO_4–EtOH gives *Et*$_2$ *α-ketoadipate-*m-*carbethoxyphenylhydrazone*, m.p. 125—127°, which in boiling 1 : 5 (vol.) H_2SO_4–EtOH gives *Et β-2 : 4-* (**III**), m.p. 105—106°, and *β-2 : 6-dicarbethoxyindole-3-propionate* (**IV**), m.p. 113°. Structures are proved as follows. CrO_3 in AcOH + a little H_2O at 25—30° oxidises (**III**) and (**IV**) to *Et γ-keto-γ-2-*(*ethyl oxalamido*)*-6-* (**V**), m.p. 84—86°, and *-4-carbethoxyphenyl-*n*-butyrate* (**VI**), m.p. 97—99°, hydrolysed by H_2SO_4–EtOH to Et γ-keto-γ-2-amino-4- (**VII**), a colourless oil, and *-6-carbethoxyphenyl-*n*-butyrate* (**VIII**), yellow, m.p. 87—88° [Bz derivative, m.p. 86—88°, hydrolysed by alkali to a (?) quinoline derivative, sinters and darkens at 210°], respectively. Hot 10% aq. KOH hydrolyses (**VIII**) to *γ-keto-γ-2-amino-4-carboxyphenyl-*n*-butyric acid*, yellow, m.p. 250° (block) or partially in a bath at 215° (resolidifies), but converts (**VII**) into the corresponding *6-*CO_2H*-acid*, sinters 168°, m.p. 180° (gas), with some *1 : 3-diketo-4-aminohydrindene-2-acetic acid*, sinters 192°, m.p. 202° (decomp.). Alkali converts (**VI**) into (?) 4-hydroxy-2 : 7-dicarboxyquinoline-3-acetic acid, sinters and darkens at >255°. Alcoholysis of (**VI**), diazotisation (OBu·NO), and then boiling gives *Et 4-hydroxy-7-carbethoxycinnoline-3-acetate*, m.p. 168–171°; similar treatment of (**V**) gives *γ-keto-γ-2-ethoxy-6-carboxyphenyl-*n*-butyric acid*, m.p. 166—168°. Attempted Dieckmann reactions with (**III**) failed. R. S. C.

Antimalarials. I. Veratrole group. K. C. Frisch and M. T. Bogert (*J. Org. Chem.*, 1943, **8**, 331—337).—3 : 4 : 5 : 1 : 2-$(NO_2)_3C_6H(OMe)_2$, m.p. 143° (lit. 144—145°), obtained from veratrole (room temp.; slowly; then 100°) or 6 : 3 : 4 : 1-NO_2·$C_6H_2(OMe)_2$·CHO (room temp.) by 1 : 1 conc. HNO_3–conc. H_2SO_4, gives with Sn–conc. HCl at 100° 3 : 4 : 5 : 1 : 2-$H_2)_3C_6H(OMe)_2$ (70%), m.p. 150—152° (*picrate*, m.p. 86°). 4 : 5 : 1 : 2-$(NO_2)_2C_6H_2(OMe)_2$ with H_2–Pd-black in EtOH at 3 atm. gives 5 : 1 : 2 : 4-NO_2·$C_6H_2(OMe)_2$·NH_2 (70—75%), but both NO_2 of *o-* and *m*-$C_6H_4(NO_2)_2$ and 2 : 4 : 1-$(NO_2)_2C_6H_3$·NH_2 are reduced. 1 : 2 : 4-$(OMe)_2C_6H_3$·NH_2, similarly obtained from the NO_2-compound, gives by a Skraup reaction 6 : 7-dimethoxyquinoline, b.p. 164°/2·3 mm. [*hydrochloride*, m.p. 222° (uncorr.); *methylmethosulphate*, +H_2O, m.p. 232° (decomp.); *methiodide*, m.p. 242° (decomp.)], which with fuming HNO_3 in oleum at 0—10° gives 5 : 8-*dinitro-*, m.p. 155°, reduced by, best, $SnCl_2$–HCl at room temp., to 5 : 8-*diamino-6 : 7-dimethoxyquinoline* (85%), b.p. 170°/0·2 mm. (picrate, m.p. 185—186°; *dihydrochloride*, m.p. 186—187°). With (CH_2·CO)$_2$O, (:CH·CO)$_2$O, or *o*-C_6H_4(CO)$_2$O in boiling COMe. this gives 5 : 8-*di-succin-*, m.p. 159—160° (decomp.), *-malein-*, m.p. 219—220° (decomp.), or *-phthal-amido-6 : 7-dimethoxyquinoline* (**I**), m.p. 173—175°, respectively; with (CH_2·CO)$_2$O at 120° or *o*-C_6H_4(CO)$_2$O in boiling dioxan it gives 5 : 8-*di-succin-*, m.p. >310° (block; sublimes), and *-phthal-imido-6 : 7-dimethoxyquinoline*, m.p. 236—238° (decomp.; block) [also obtained from (**I**) in boiling EtOH], respectively, but no dimalcinimide can be obtained. M.p. are corr. R. S. C.

Preparation of iodine-containing contrast substances. III. Structure of "choloselectan." W. Baker, H. Sansbury, and (in part) W. H. C. Simmonds (*J.C.S.I.*, 1943, **63**, 193—194).—*p*-OH·C_6H_4Ac (**I**) (from PhOAc and $AlCl_3$ in $PhNO_2$), treated with ICl in dil. HCl, gives 4 : 3 : 5 : 1-OH·$C_6H_2I_2$·COMe (**II**), which with 5-iodoisatin (**III**) (from isatin and ICl in boiling AcOH) gives 6 : 3′ : 5′-tri-iodo-4′-hydroxy-2-phenylquinoline-4-carboxylic acid (**IV**), m.p. 271° (lit., decomp. 215—226°). Refluxing the K salt of (**II**) with Cl·[CH_2]$_2$·OH in COMeEt gives 3 : 5 : 4 : 1-$C_6H_2I_2$(O·[CH_2]$_2$·OH)·COMe (**V**), which with (**III**) gives (**IV**), m.p. 274°. Reduction of (**IV**) by 1½ atm. H_2 and Raney Ni gives 4′-hydroxy-2-phenylquinoline-4-carboxylic acid [Ac derivative, m.p. 212—213°, identical with a specimen prepared from isatin and (**I**)]. (**V**) is hydrolysed to (**II**) by KOH–EtOH. Choloselectan (**VI**) is believed to be very impure (**IV**), prepared from (**V**). Since (**IV**) gives no *X*-ray visualisation of the gall bladder, the reputed effect of (**VI**) must be due to an impurity. S. A. M.

Nature of the amino-group in aminoacridines. I. Evidence from electrometric studies. A. Albert and R. Goldacre. **II. Evidence from chemical reactions.** A. Albert and B. Ritchie (*J.C.S.*, 1943, 454—458, 458—462).—I. The relative basicities of acridine, 1-, 2-, 3-, 4, and 5-hydroxy-, 1-, 2-, 3-, 4-, and 5-amino-, 1-, 2-, 3-, 4-, and *5-acetamido-acridine*, m.p. 276° (corr.), 2-, 3-, 4-, and 5-amino-10-methylacridinium hydroxide, *2-aminoacridine-7-carboxylic acid* (**I**), decomp. 200°, -7-sulphonic acid, and -7-sulphonamide, are examined, and it is found that the structure of 2- and 5-aminoacridines permits a greater degree of resonance in the ion than occurs in the non-ionised base. Hence, these isomerides show an abnormally high degree of ionisation, an effect that parallels their high biological activity. The properties of the other isomerides suggest that they are fairly normal NH_2-derivatives of acridine. Condensation of 4 : 2 : 1-NO_2·C_6H_3Cl·CO_2H and *p*-NH_2·C_6H_4·CO_2H (Cu–NaOAc) gives *5-nitrodiphenylamine-2 : 4′-dicarboxylic acid*, m.p. 281°, which with $POCl_3$ affords *2-nitroacridone-7-carboxylic acid*, m.p. >360°. Reduction (Al–Hg) of this acid yields the 2-aminoacridan acid, which is oxidised ($FeCl_3$) to (**I**).

II. Examination of the chemical reactions of the five monoaminoacridines reveals no correlation as striking as that between ionisation and antisepsis. The biologically outstanding isomerides (5-, 2-, and 1-) show the greatest chemical individuality, particularly the first, which behaves distinctively on diazotisation, alkaline hydrolysis, hydrogenation, and reaction with aldehydes and with MeI. Because of the highly electrophilic nature of the acridine nucleus, the NH_2 is readily detached from the salts of all the isomerides by NH_2Ph and by acid at 160°. Condensation with aldehydes gives 1-, m.p. 151°, 3-, m.p. 148° (uncorr.), and *4-benzylidene-*, m.p. 182°, and *2-salicylidene-aminoacridine*, m.p. 236°, and *2-nitrodiphenylamine-2′-aldehyde*, m.p. 120° (uncorr.). 5-Aminoacridine (**II**) is the only compound which affords a satisfactory product, 5-amino-10-methylacridinium iodide, with MeI. The appropriate acetamidoacridine when methylated (*p*-C_6H_4Me·SO_3Me) and treated with HBr gives 2- (+H_2O), m.p. 243°, 3-, 4-, m.p. 267° (uncorr.), and *5-amino-10-methylacridinium bromide*, m.p. ~305° (decomp.). *5-Amino-5-hydroxy-10-methylacridan*, obtained from the bromide, affords at 130° *5-imino-10-methylacridan*, m.p. 134—136° (sealed tube). Reduction (fresh $FeCO_3$) of *3-nitro-5-aminoacridine hydrochloride* leads to 3 : *5-diaminoacridine*, m.p. 229—230° (sealed tube). 5-Phenoxyacridine with NH_3MeCl and PhOH gives *5-methylaminoacridine*, m.p. 173—174° (sealed tube); *5-dimethylaminoacridine hydrochloride*, m.p. 275° (decomp.), is similarly prepared. The two foregoing bases and (**II**) are hydrolysed (KOH–EtOH), to the OH-compound but not the 1-, 2-, 3-, and 4-NH_2-derivatives; the latter are, however, hydrolysed by HCl [*4-hydroxyacridine*, m.p. 250° (decomp.), and 2-derivative, m.p. 285° (sealed tube)]. Treatment of the amine hydrochloride with NH_2Ph affords 1-, m.p. 191°, 2-, m.p. 238°, 3-, m.p. 236°, 4-, m.p. 220° (decomp.), and *5-anilinoacridine*, m.p. 230·5°. Hydrogenation affords the corresponding acridans [3-aminoacridan, m.p. 187—188° (lit. 191—192°)]. M.p. are corr. unless otherwise stated. F. R. S.

Basic esters of polynuclear carboxylic acids.—See A., 1944, II, 15.

Hydantoins.—See B., 1943, II, 342.

Derivatives of piperazine. XX. Monoalkylation of piperazine by alkylene oxides. L. J. Kitchen and C. B. Pollard (*J. Org. Chem.*, 1943, **8**, 338—341; cf. A., 1941, II, 149).—By use of an excess of piperazine in, *e.g.*, MeOH at 80°, $(CH_2)_2O$, αβ-epoxy-propane and

-*iso*butane give good yields of mono(hydroxyalkyl) compounds. Thus are prepared 1-*β*-hydroxy-ethyl-, b.p. 119·2°/10 mm. [dihydrochloride, m.p. 188·6—189·6° (lit. 182—183°); picrate, m.p. ~245° (decomp.) (lit. 247—248°); phenylthiocarbamide derivative, m.p. 114·9—115·3°], -*n*-propyl-, b.p. 108·5°/10 mm. [*dihydrochloride*, m.p. ~237·3° (decomp.); picrate, m.p. 174·5—177·5°; phenylthiocarbamide derivative, m.p. 144—144·5°], and -*iso*butyl-, m.p. 80·2—80·5°, b.p. 106°/10 mm. [dihydrochloride, decomp. ~215°, slowly at <215°; picrate, m.p. 257° (decomp.); phenylthiocarbamide derivative, m.p. 129·3—129·5°], and 1 : 4-di-*β*-hydroxy-ethyl-, m.p. 134·3—150°, -*n*-propyl-, m.p. 116·7—117·9° (lit. 115—116°) [dihydrochloride, m.p. 223·7—224·7° (decomp.)], and -*iso*butyl-piperazine, m.p. 101·5—102·5°, M.p. are corr. R. S. C.

Barbituric acids.—See B., 1943, III, 280.

Cinnolines. II. Influence of substituents on the Widman–Stoermer and the Pschorr reaction. J. C. E. Simpson (*J.C.S.*, 1943, 447—452).—A review of the published evidence respecting cyclisation of diazotised *o*-aminoarylethylenes of type $NH_2{\cdot}C_6H_4{\cdot}\overset{(\alpha)}{C}R{\cdot}CHR'$ leads to the conclusion that the Widman–Stoermer cinnoline synthesis is inhibited when R = H or CO_2H and R′ = aryl or another negative group such as CO_2H, CO_2Et, or CN. It is now shown that the attachment of a Ph group to $C_{(\alpha)}$ is a dominant factor favouring cinnoline formation. The Grignard compound from 1-$C_{10}H_7{\cdot}CH_2Cl$ with *o*-$NH_2{\cdot}C_6H_4{\cdot}COPh$ gives a mixture of $(CH_2{\cdot}C_{10}H_7\text{-}1)_2$, m.p. 161—161·5° (lit. 100°), and *α-phenyl-α-(2-aminophenyl)-β-(1′-naphthyl)-ethylene*, m.p. 182—183°, and its *isomeride* (**I**), m.p. 144—145°; the intermediate aminocarbinol with Ac_2O affords the *acetamidocarbinol*, m.p. 175—176°. The diazonium solution from (**I**) with NaOAc and Cu (Pschorr reaction) yields *2-phenylchrysene*, m.p. 192—192·5°, whilst when diluted at room temp. it is cyclised to *4-phenyl-3-(1′-naphthyl)cinnoline*, m.p. 178—179°. $CH_2Ph{\cdot}MgCl$ with *o*-$NH_2{\cdot}C_6H_4{\cdot}COPh$ gives *phenyl-2-aminophenylbenzylcarbinol*, m.p. 150—150·5°, dehydrated (20% H_2SO_4) to *α-(2-aminophenyl)-αβ-diphenylethylenes*, m.p. 113—114° and 102—104° (geometrical isomerides), which are cyclised following diazotisation to 3 : 4-*diphenylcinnoline*, m.p. 149—150°. $Ph{\cdot}[CH_2]_2{\cdot}Br$ similarly affords *phenyl-2-aminophenyl-β-phenylethylcarbinol*, m.p. 97—98° (N-*Ac* derivative, m.p. (68—168·5°), *α-phenyl-α-(2-aminophenyl)-β-benzylethylene*, m.p. 108—109°, and *4-phenyl-3-benzylcinnoline*, m.p. 116·5—118°. Mg allyl bromide with *o*-$NH_2{\cdot}C_6H_4{\cdot}COPh$ gives a mixture of a basic *substance*, $C_{15}H_{17}ON$, m.p. 79—80° [isomerised (5% H_2SO_4) to a *substance*, m.p. 129·5—130·5°], and *phenyl-2-aminophenylallylcarbinol*, m.p. 70—72° (N-*Ac*, m.p. 129—130°, and N-*Bz* derivatives, m.p. 173·5—175°). Condensation ($C_5H_{11}N$) of 1 : 2 : 4-$C_6H_3Me(NO_2)_2$ with furfuraldehyde, piperonal, and vanillin yields *products*, $C_{17}H_9O_5N_2$, m.p. 135—136°, $C_{15}H_{10}O_6N_2$, 179·5—180·5°, and $C_{15}H_{12}O_6N_2$, 191—191·5°, respectively. Reduction of the furfurylidene compound with Fe–AcOH and H_2S–aq. NH_3 affords respectively *α-nitroaminophenyl-β-(2-furyl)ethylenes*, m.p. 130·5—131·5° (N-*Ac* derivative, m.p. 214—215°) and 86—88° (N-*Ac* derivative, m.p. 168·5—169·5°), from the diazo-solutions of which cryst. products could not be obtained. From MgMeI and 5-chloro-2-amino-4′-hydroxy- and -2′-hydroxy-5′-methyl-benzophenone, the corresponding *carbinols*, m.p. 173—174°, and 117—118·5°, have been obtained (cf. Simpson *et al.*, A., 1942, II, 273). F. R. S.

Tetrazole.—See B., 1943, III, 280.

Condensation of aminoantipyrine. III. (I) Synthesis of methylrubazoic acid. E. Emerson and L. C. Beegle (*J. Org. Chem.*, 1943, **8**, 429—432). *Methylrubazoic acid* (**I**),

m.p. 175—176°, is prepared by oxidising an equimol. mixture of aminoantipyrine (**II**) and 1-phenyl-3-methylpyrazol-5-one or by condensing (**I**) with 4-keto-1-phenyl-3-methylpyrazol-5-one. The reactions also establish the structures of many of the other coloured products formed in the positive test with (**II**). Repetition of the work of Proscher (A., 1902, i, 505) shows that the product described by him as (**I**) is greatly contaminated by products of high mol. wt. probably due to the nitrosoantipyrine used. H. W.

Properties of *m*-nitrodibenzoylmethane.—See A., 1944, II, 17.

Bacterial chemotherapy. I. Synthesis of N^1-substituted sulphanilamides. II. Synthesis of possible intestinal antiseptics of the sulphanilamide group. III. Synthesis of possible lipophilic chemotherapeuticals of the sulphonamide group. S. Rajagopalan (*Proc. Indian Acad. Sci.*, 1943, **18**, **A**, 100—103, 104—107, 108—112).—I. $NHAc{\cdot}C_6H_4{\cdot}SO_2Cl$ is condensed in C_5H_5N with various amines, and the Ac hydrolysed by hot dil. HCl. The following are described, in addition to those mentioned in A., 1942, II, 289: *ω-N⁴-acetylsulphanilamidoaceto-phenone*, m.p. 151—152° (decomp.), and *-α-naphthone*, m.p. 202—204° (decomp.); the *hydrochlorides* of *ω-sulphanilamidoaceto-phenone*, m.p. 200—202° (decomp.), and *-α-naphthone*, sinters 185°, m.p. 189° (decomp.); *5-sulphanilamidobenztriazole*, m.p. 135—137°; *5-N⁴-acetylsulphanilamidoindazole*, m.p. 262° (decomp.); *1-sulphanilylindole*, m.p. 159° (decomp.) (*N⁴-Ac* derivative, m.p. 146—147°); *3-N⁴-acetylsulphanilamidoindotriazine* [-1 : 2 : 4-*triazacarbazole*], m.p. 261—262°. The m.p. of *3-N⁴′-acetylsulphanilamido-1 : 2 : 4-triazole* is now given as 210° (decomp.). The following Schiff's bases are prepared by boiling mol. proportions of an aldehyde and a sulphonamide in EtOH until crystals separate: *m-hydroxy-*, m.p. 138°, and *o-nitro-benzylidenesulphanilamide*, m.p. indefinite; o-, m.p. indefinite, and *m-nitrobenzylidenesulphathiazole*, m.p. 220—222° (decomp.); recrystallisation is impossible.

II. Chiefly by the action of alkyl or aralkyl halides or alkyl sulphates on sodio-sulphanilamido-derivatives of heterocyclic compounds, a series of compounds insol. in alkali, therefore not likely to be absorbed in the intestine, and so expected to be particularly useful in infections of the intestinal tract, have been prepared. The following are described: *3-methyl-*, m.p. 196—198°, and *3-ethylsulphanilimido-2 : 3-dihydrothiazoline*, m.p. 181—182° (decomp.); *N¹-phenyl-*, glassy at 156°, clearing at ~185° (*N⁴-Ac* derivative, m.p. 230°), and *N¹-allyl-sulphathiazoline*, softens 187°, m.p. 186—189° (*N⁴-Ac* derivative, sinters 176°, m.p. 179—181°); *2-sulphanilimido-*, m.p. 234° (decomp.) (*N⁴-Ac* derivative, m.p. 215—218°), and *2-p-nitrobenzylaminobenzenesulphonimido-1-p-nitrobenzyl-1 : 2-dihydropyridine*, m.p. 208—210°; *2-sulphanilimido-3-p-nitrobenzyl-*, m.p. 199—200° (decomp.), and *-3-m-nitrophenacyl-2 : 3-dihydrothiazole*, m.p. 238—239° (*N⁴-Ac* derivative, m.p. 216—218°).

III. Some members of the sulphonamide group known to be active in coccal infections are acylated, with a view to rendering them lipophilic, and thus useful for mycobacterial infections. By condensing sulphonamides and acyl chlorides in C_5H_5N, the following additional compounds are prepared (cf. A., 1943, II, 144); *N⁴-n-octoylsulphapyridine*, m.p. 213—214°; *N⁴N¹-diacylsulphapyridines*: acyl = *Ac*, m.p. 194°, n-*butyryl*, m.p. 163°, n-*hexoyl*, m.p. 155—157°, n-*octoyl*, m.p. 135°, *Bz*, m.p. 217°, cyclo*hexoyl*, m.p. 193—195°, *cinnamoyl*, m.p. 196—198°; *N⁴-furoylsulphathiazole*, decomp. >240°; *N⁴-n-octoylsulphanildimethylamide*, m.p. 79—82°; *N⁴-n-hexoyl-*, m.p. 215°, *N⁴-n-heptoyl-*, m.p. 173—174°, and *N⁴-n-octoyl-2-sulphanilimido-3-methyl-2 : 3-dihydrothiazole*, m.p. 153—154°; *N⁴-n-butyryl-*, m.p. 248—250° (decomp.), and *N⁴-n*-hexoyl-*N¹-p*-nitrophenylsulphanilamide, m.p. 152° (lit. 225°); *N⁴-n-butyryl-*, m.p. 235—236°, and *N⁴-n-hexoylsulphanilylsulphanilamide*, m.p. 184—186°; 2-, m.p. 226—228° (decomp.), and *4-N⁴′-butyrylsulphanilamidobenzoic acid*, m.p. 224—226°. The m.p. of 2-sulphanilamidobenzoic acid is ~215° (decomp.) (lit. 225°), and of its 4-isomeride is 181—182° (lit. 202°, 198—200°). The following are prepared by the action of Me_2SO_4 on aq. alkaline solutions of the corresponding *N¹*-unsubstituted *N⁴*-acylsulphonamides: *2-N⁴-n-butyryl-*, m.p. 213°, and *2-N⁴-n-hexoyl-sulphanilimido-1-methyl-1 : 2-dihydropyridine*, m.p. 213—215°; *2-N⁴-n-hexoyl-*, m.p. 201—203°, and *2-N⁴-n-heptoylsulphanilimido-3-methyl-2 : 3-dihydrolthiazoline*, m.p. 170°. S. A. M.

Photographic products.—See B., 1943, II, 400.

Thiazinocyanines. III. Carbocyanines containing the *peri*-naphtha-1 : 3-thiazine nucleus. (Miss) F. M. Hamer and R. J. Rathbone (*J.C.S.*, 1943, 487—491).—The observations of Joy *et al.* (A., 1937, II, 37) have been confirmed. 2-Methyl*peri*naphtha-1 : 3-thiazine methiodide (**I**), m.p. 177° (decomp.) [lit. m.p. 222—230° (decomp.)], with $CH(OEt)_3$ in C_5H_5N gives bis-2-(3-methyl-*peri*naphtha-1 : 3-thiazine)trimethincyanine iodide, m.p. 223° (decomp.), without $CHCl_3$ of crystallisation; the *methosulphate*, m.p. 232° (decomp.), is similarly obtained from the corresponding methomethylsulphate. Bis-2-(3-ethyl*peri*naphtha-1 : 3-thiazine)trimethincyanine iodide, m.p. 212° (decomp.) [lit. m.p. 243° (decomp.)], has also been obtained without $CHCl_3$ of crystallation. *β*-Anilinoacraldehyde anil hydrochloride and (**I**) with KOAc–Ac_2O give *bis-2-(3-methyl*peri*-naphtha-1 : 3-thiazine)pentamethincyanine iodide*, m.p. 183° (decomp.). 2-Methyl*peri*naphtha-1 : 3-thiazine (**II**) and 2-*β*-acetanilidovinylbenzoxazole ethiodide at 125° afford *trimethin*[2-(3-*ethyldihydrobenzoxazole*)][2-(*perinaphtha-1 : 3-thiazine*)], m.p. 165—168° (decomp.) [*hydrochloride*, m.p. 200° (decomp.)]. By condensing (**II**) with the appropriate reagent, the following are obtained: *trimethin*[2-(3-*ethyldihydro-4 : 5-*, m.p. 190° (decomp.), and *-6 : 7-benzbenzoxazole*)]-, m.p. 155° (decomp.), *-benzthiazole*)], m.p. 196° (decomp.), *-4 : 5-*, m.p. 215° (decomp.), and *-6 : 7-benzbenzthiazole*)]-[2-(*perinaphtha-1 : 3-thiazine*)], m.p. 212° (decomp.) [*hydrochloride*, m.p. 218° (decomp.)]. *2-(3-Ethylbenzoxazole)*][2-(3-*methyl-*, m.p. 202° (decomp.), and *-ethyl-perinaphtha-1 : 3-thiazine)]trimethincyanine iodide*, m.p. 173° (decomp.), are obtained from the carbocyanine with MeI and EtI respectively. *2-p-Dimethylaminostyrylperinaphtha-1 : 3-diazine*, m.p. 213° (decomp.), its *hydriodide*, m.p. 235—240° (decomp.), and *methomethylsulphate*, m.p. 116° (decomp.), are obtained from *p*-$NMe_2{\cdot}C_6H_4{\cdot}CHO$ and (**II**) or its appropriate derivative. The carbocyanines and dicarbocyanine from (**II**) are abnormal in being decolorised by alkali. Absorption data for MeOH solutions of the dyes are recorded and comparisons made with the dihydro-1 : 3-thiazine, 2 : 4-benzthiazine, and naphthathiazole series. F. R. S.

VII.—ALKALOIDS.

***Senecio* alkaloids. I. Rosmarinine.** (Miss) M. F. Richardson and F. L. Warren (*J.C.S.*, 1943, 452—454).—Rosmarinine (**I**), isol-

ated originally from *S. rosmarinifolius*, Linn., has now been found in other species. *S. hygrophilus*, R. A. Dyer and C. A. Sm., is con-sp. with "*S. adnatus*," DC., but the alkaloid content varies; (I), platyphylline, and an *alkaloid*, $C_{18}H_{27}O_6N$, m.p. 175—176° (corr.), $[\alpha]_D^{25}$ −62·4° in MeOH, have been isolated as sole constituents or as mixtures, depending on stage of growth, season, and (South African) district. Hydrolysis of (I) gives *rosmarinecine*, $C_8H_{15}O_2N$ (probably 3′ : 4-dihydroxy-3-hydroxymethylpyrrolizidine), m.p. 171—172° (corr.), $[\alpha]_D^{25}$ −118·5° [*methiodide*, m.p. 195° (corr.)], and *senecic acid*, m.p. 151° (corr.), $[\alpha]_D^{25}$ +11·8° in EtOH, neither compound having previously been obtained cryst. Platynecic acid is senecic acid lactone. F. R. S.

Curare alkaloids from *Chondrodendron tomentosum*.—See A., 1944, III, 88.

VIII.—ORGANO-METALLIC COMPOUNDS.

Diazonium borofluorides. IV. Preparation of copper aryl compounds. F. A. Bolth, W. M. Whaley, and E. B. Starkey (*J. Amer. Chem. Soc.*, 1943, **65**, 1456—1457; cf. A., 1942, II, 336).—The reaction, $ArN_2 \cdot BF_4 + 2Cu \rightarrow CuAr + N_2 + CuF + BF_3$, is realised for Ar = Ph, *p*- and *o*-$NO_2 \cdot C_6H_4$, and *o*-tolyl in C_6H_6 or PhMe at ~70—85°. For CuPh and Cu·C_6H_4Me-*p* (I) analysis of the solution shows yields of CuAr to be 4—8% and 30—35%, respectively. CuPh and (I) do not react with Michler's ketone. CuPh, but not (I), reacts with BuBr in C_6H_6 or PhMe. Cu aryls are hydrolysed at once by moisture and with solid CO_2 give amorphous compounds which react at once with air. They are pptd., probably as complexes, by dioxan or Et_2O. C_5H_5N ppts. *Cu Ph* and p-*nitrophenyl tripyridine* (II), which are blue and stable in air, even at 110°, but in boiling H_2O Cu is pptd. from (II). CuPh and Cu·$C_6H_4 \cdot NO_2$-*o* with $CH_2Cl \cdot COCl$ give good yields of $CH_2Cl \cdot COAr$. The significance of these results for various diazonium reactions is noted. R. S. C.

Solvents in organometallic chemistry. A. H. Haubein (*Iowa State Coll. J. Sci.*, 1943, **18**, 48—50; cf. C., 1944, Part I).—The orders of stability of LiR compounds in Et_2O and of R_2O compounds in presence of LiBu, $LiBu^v$, and Li·CHMeEt were determined by difference between the total and inorg. base formed on hydrolysis. Cleavage by Li compounds of ethers containing $NR_2 \cdot CH_2 \cdot$ can be used to introduce this group into a large no. of mols. F. R. G.

Mercurated aliphatic nitriles.—See B., 1943, III, 280.

Selenium compounds.—See B., 1943, II, 343.

Borohydrides of gallium.—See A., 1944, I, 22.

IX.—PROTEINS.

Nature of formaldehyde compounds of proteins. K. H. Gustavson (*Kolloid-Z.*, 1943, **103**, 43—54).—The tanning effect of CH_2O on proteins is discussed. Fibrous proteins, *e.g.*, collagen (I), are more easily studied than H_2O-sol. proteins, since they have measurable properties altered by CH_2O treatment. Properties studied are temp. of contraction, swelling in H_2O, and degradation by trypsin. In dil. CH_2O solutions irreversible CH_2O fixation is due to the ε-NH_2-groups of lysine in the pH range 5—8, and the NH_2-groups of arginine at pH >8. In conc. solutions secondary reactions occur. CH_2O combines with partly deaminated (I) freed from primary NH_2 groups, but does not have a tanning effect. Thus the CH_2O attached to NH_2-groups of arginine residues does not stabilise (I) chains by cross-linking; tanning by CH_2O results from formation of cross-linkings between ε-NH_2-groups of lysine in neighbouring chains. In acid solutions native (I) shows a tanning effect at high CH_2O concn., but deaminated (I) is unchanged. CH_2O fixation is a slow reaction in this case. CH_2O is also taken up by peptide groups, but is not then involved in cross-linking and stabilising the structure. CH_2O is also effective in org. solvents. R. H. F.

Complex formation between synthetic detergents and proteins. F. W. Putnam and H. Neurath (*J. Biol. Chem.*, 1943, **150**, 263—264; cf. Lundgren *et al.*, A., 1943, III, 838).—Cryst. horse serum-albumin is pptd. on the acid side (complex formation but no pptn. occurs on the alkaline side) of the isoelectric point by Na dodecyl sulphate (I) when the ratio of protein to (I) ranges from 5 : 1 to 2·5 : 1, all the (I) being bound by the protein. Excess of (I) causes dissolution of the pptd. complex, but protein recovered from the solution does not differ in solubility and electrophoretic properties from that recovered from the ppt. The max. concn. of (I) required for complete pptn. (144 mols. per g. of protein × 10^5) corresponds closely with the total acid-binding capacity of the protein. Protein recovered from the complex after removal of detergent with $BaCl_2$ is electrophoretically homogeneous but the hydrodynamic vol. is diminished to 75% of the original val. and the mobility at pH 7·6 is increased slightly. Measurements of viscosity show that denaturation occurs on both sides of the isoelectric point. The denaturing power of (I) is that of $CO(NH_2)_2$ or guanidine. W. McC.

Constitution of proteins. Demonstration [of the presence] of porphyrin complexes, pyridine rings, and elementary [characteristic ?] complexes. N. Troensegaard (5 *Nordiske Kemikermøde*, 1939, 232).—Proteins are acetylated and/or hydrogenated in H_2O-free solvents (no details) to protect them during hydrolysis. The product is hydrolysed in the cold, giving acidic and basic fractions, the latter containing piperazines, pyrroles, and (from some proteins) piperidine. The acid fraction contains complexes characteristic of the original protein: gliadin gives $C_{10}H_{14}O_3N_2$ or $C_{10}H_{12}O_3N_2$. M. H. M. A.

Coloured metallic complexes of keratin and fibroin. B. Nilssen (5 *Nordiske Kemikermøde*, 1939, 234—236).—The coloration given with HNO_2 and keratin or fibroin is due to conversion of tyrosine residues into *o*-quinonemonoxime residues which give lakes with heavy metals. M. H. M. A.

X.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Crystalline barium acid heparinate. M. L. Wolfrom, D. I. Weisblat, R. J. Morris, C. D. DeWalt, J. V. Karabinos, and J. McLean (*Science*, 1943, **97**, 450).—The following molar ratios were established: anhydrohexosamine : anhydrohexuronic acid : SO_3 : Ba = 2·0 : 1·9 : 6·0 : 3·0; N : S : Ba = 2 : 6 : 3. Summation of these data (89%) does not preclude the possible presence of another constituent. *d*-Glucosamine, the NH_2-group of which is not acetylated and not free, was identified in the hydrolysate of the acid Ba salt. Repeated crystallisation from warm, dil. AcOH destroys the anticoagulant power, and is accompanied by the appearance of a free NH_2-group. Prolonged drying and dil. H_2O_2 also inactivate the salt. E. R. R.

Derivatives of lonchocarpic acid. H. A. Jones and H. L. Haller (*J. Org. Chem.*, 1943, **8**, 493—496).—In spite of their closely related origin, no close relationship exists between lonchocarpic acid (I) and rotenone (II). It is quite probable that the characteristic chroman-chromanone system present in (II) is absent from (I). (I), obtained from an unknown species of *Lonchocarpus*, has usually m.p. 203—204° (corr.) when cryst. from EtOAc and 220—221° (corr.) when cryst. from EtOH. It is converted by NaOAc and boiling Ac_2O into *diacetyl-lonchocarpic acid*, m.p. 154°, which is insol. in aq. alkali and when hydrolysed by alkali gives (I), alkali-insol. material, and alkali-sol. resin whereas it affords an unpurified product with KOAc in abs. EtOH. It is indifferent towards CH_2N_2 in MeOH or Et_2O. Methylation of (I) by CH_2N_2 in Et_2O gives *methyl-lonchocarpic acid*, m.p. 210—212°, whereas in MeOH the product is *dimethyl-lonchocarpic acid*, m.p. 150—151°; both products are insol. in alkali and do not yield an alkali-sol. product when hydrolysed by KOH–MeOH. Me_2SO_4 appears to give a mixture of mono- and di-acid. Catalytic hydrogenation (PtO_2 in EtOH) of (I) leads to *tetrahydrolonchocarpic acid*, m.p. 239—240° (*diacetate*, m.p. 192—192·5°; *Me*., m.p. 211—212·5°, and *Me*$_2$, m.p. 166—167°, derivatives). Oxidation of (I) by I in EtOH containing KOAc does not give a recognisable product, whereas *p*-OH·$C_6H_4 \cdot CO_2H$ is obtained in ~25% yield by use of H_2O_2 in alkaline solution. PCl_5 and $SOCl_2$ do not react with (I). H. W.

Scandenin, a constituent of the roots of *Derris scandens*. E. P. Clark (*J. Org. Chem.*, 1943, **8**, 489—492).—Extraction of the powdered air-dried roots of *D. scandens* gives *scandenin* (I), $C_{26}H_{26}O_6$, m.p. 231°, lonchocarpic acid, m.p. 223° (corr.), softens at 200—205°, and small quantities of a third substance which by reason of its solubility in alkali, its m.p. 190°, and behaviour in the Durham test is regarded as robustic acid. Rotenone is not observed and the substances isolated do not appear to belong to the rotenone group of fish poisons. (I) contains 1 OMe and 2 OH since it readily gives a *diacetate*, m.p. 150°, and is converted by CH_2N_2 into a *Me*$_2$ *ether*, m.p. 129°, in poor yield. Although an oxime or semicarbazone could not be obtained it probably contains a *p*-OH·$C_6H_4 \cdot CO$ since it gives the corresponding acid when oxidised by alkaline H_2O_2. It absorbs ~3 mols. of H_2 when hydrogenated in EtOH containing PtO_2. It is somewhat acidic, dissolving in dil. alkalis. It gives a relatively sparingly sol. Na and K salt. It fails to give the reaction for a 2 : 2-dimethyl-Δ^3-chromene system.

Helvolic acids $C_{32}H_{44}O_8$, m.p. 212°, $[\alpha]_D^{20}$ −49·4° in CHCl$_3$ (Me ester, m.p. 261°).—See A., 1943, III, 917.

Aspergillic acid, $C_{12}H_{20}O_2N_2$.—See A., 1943, III, 916.

***X*-Ray diffraction data on ferritin and *apo*ferritin.**—See A., 1944, I, 5.

XI.—ANALYSIS.

Spectrophotometric analysis of multicomponent mixtures.—See A., 1943, I, 319.

For abstracts on analysis, see C., 1944, Part I.

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A II—Organic Chemistry.

FEBRUARY, 1944.

I.—ALIPHATIC.

Isomorphous replaceability of bivalent atoms and ψ-atoms in organic compounds. A. Lüttringhaus (*Ber.*, 1940, **73**, [*B*], 1022—1023).—A reply to Bruni (A., 1943, II, 308). Valency angles are considered. R. S. C.

Behaviour of the free *n*-propyl radical. G. Semerano, L. Riccoboni, and L. Gotz (*Z. Elektrochem.*, 1941, **47**, 484—486).—From the amounts of C_3H_6 and C_3H_8 produced by the thermal decomp. of $AgPr^a$ it is concluded that ~77% of the Pr^a radicals initially formed disproportionate to C_3H_6 and C_3H_8 and the remainder dimerise to *n*-C_6H_{14}. J. F. H.

Optical rotation and atomic dimension. The four optically active β-halogenopentanes. D. H. Brauns (*J. Res. Nat. Bur. Stand.*, 1943, **31**, 83—106).—The enantiomorphic modifications of pentan-β-ol (I) have been prepared in the pure state and the lævorotatory isomeride has been converted into dextrorotatory β-Cl-, -Br-, and -I-derivatives. Lævorotatory β-CHMePr^aF is obtained from the dextrorotatory β-bromo- or -iodo-pentane and AgF. The derivatives obtained by halogenation of the alcohol with $PHal_3$ have higher [α] than those obtained by use of HHal. The purity of the Cl-, Br-, and I-derivatives is ~70—80%; the optical purity of the F-derivative, the prep. of which involves another Walden inversion, is less. The relative amounts of the isomeric modifications are determined by the purity of the alcohol obtained by hydrolysis and the relative optical rotations of the pure F-, Cl-, Br-, and I-derivatives are calc. All halogen derivatives of (I) of like configuration have the same sign of optical rotation. The difficulty of obtaining optically pure compounds on account of incomplete Walden inversion (partial racemisation) prevents an adequate check of the rule according to which for compounds in which the halogen is directly attached to the asymmetric C the differences of sp. rotations of the *d*- or *l*-compounds (Cl — F), (Br — Cl), and (I — Br) have the same numerical relation as the differences of the respective at. radii of the neutral halogen atoms. The experimental data, however, in no manner contradict the rule, the deviations which are observed being plausibly explained by the incompleteness of the Walden inversion. H. W.

Hydrogenation of the triple linking. A. L. Henne and K. W. Greenlee (*J. Amer. Chem. Soc.*, 1943, **65**, 2020—2023).—CH·CAlk in liquid NH_3 are quantitatively reduced to *trans*-olefines by Na and $(NH_4)_2SO_4$ (insol. in liquid NH_3); NH_4Cl, which is sol. in liquid NH_3, gives inefficient reduction; thus, H generated from an acetylene is more efficient than H generated from NH_4^+; the function of the NH_4 salt is to regenerate the acetylene from its Na derivative. Reduction of CAlk:CAlk′ by Na and NH_4 salts is inefficient, some H_2 escaping and an excess of Na being consumed; the Na probably adds to the C:C. Catalytic hydrogenation of acetylenes to olefines is best effected by Ni–kieselguhr in EtOH at 30—80°/3 atm.; it yields mainly *cis*-olefines (cf. Campbell *et al.*, A., 1941, II, 216; 1942, II, 71). The following are prepared: Δ^α-, m.p. —102·56°, b.p. 121·37°, *trans*-Δ^β-, f.p. —87·8°, b.p. 124·94°, *trans*-Δ^γ-, f.p. —110·05°, b.p. 123·29°, and *trans*-Δ^δ-, f.p. —93·80°, b.p. 122·37°, "*cis*"-Δ^β-, f.p. —100·5°, b.p. 125·62°, "*cis*"-Δ^γ-, f.p. —137° to —138°, b.p. 122·7°, and "cis"-Δ^β-*n*-octene, f.p. —120·2°, b.p. 122·8°; "*cis*"-Δ^β-, f.p. — 141·4°, and -Δ^γ-*n*-hexene, f.p. —143·3°; "*cis*"-Δ^ε-*n*-decene, f.p. —112·8°. With Na and $(NH_4)_2SO_4$ in NH_3, $[CH_2]_3(C{:}CH)_2$ and $[CH_2]_3(C{:}CMe)_2$ give Δ^{αζ}-heptadiene, f.p. —129·35°, b.p. 90·01°, and impure *trans-trans*-Δ^{βη}-nonadiene (I), f.p. —76·2°, b.p. 150·5°. (I), prepared by Na alone, is purer and has f.p. —72·4°, b.p. 150·3°. Catalytic hydrogenation gives impure *cis-cis*-Δ^{βη}-nonadiene, a glass, b.p. 151·0°. R. S. C.

Substituted acetylenes and their derivatives. XLVI. Formaldehyde derivatives of acetylenic hydrocarbons. G. F. Hennion and E. P. Bell (*J. Amer. Chem. Soc.*, 1943, **65**, 1847—1848; cf. A., 1942, II, 327).—Adding $RCO_2{\cdot}CH_2Cl$ to finely dispersed CR′·CNa (prep. *in situ* described) in C_6H_6–N_2 and then boiling gives Δ^β-*n*-*heptinenyl acetate* (16%), b.p. 82—83°/7 mm., *propionate* (21%), b.p. 70—71°/4 mm., and *benzoate* (10%), b.p. 160—162°/2 mm., and *n*-$C_5H_{11}{\cdot}C{\cdot}C{\cdot}CH_2{\cdot}OAc$ (10%), b.p. 79—81°/6 mm.; coating of the CR′:CNa with NaCl prevents more than initial reaction. $CH_2Cl{\cdot}OAc$ does not react with CH:CNa in Et_2O or C_6H_6; $CBu^a{\cdot}CNa$ cannot be obtained sufficiently fine in Et_2O to react. $CH_2Cl{\cdot}OR$ and $CBu^a{:}C{\cdot}MgBr$ in Et_2O give Me (42%), b.p. 80—81°/29 mm., *Et* (27%), b.p. 77—78°/20 mm., and Pr^a Δ^β-n-*heptinenyl ether* (34%), b.p. 60—62°/6 mm.; $(CH_2Cl)_2O$ in presence of a little CuCl gives *di*-Δ^β-n-*heptinenyl ether* (21%), b.p. 140—142°/6 mm. CH_2Br_2 does not react with $CBu^a{\cdot}CNa$ in liquid NH_3 (gives much tar) or $CBu^a{\cdot}C{\cdot}MgBr$ in Et_2O. $CH_2{:}SO_4$, $CBu^a{:}C{\cdot}MgBr$, and a trace of CuCl in boiling Et_2O give Δ^{εθ}-n-*tridecadi-inene* (13%), b.p. 108—110°/8 mm. *d*, *n*, and [*M*] are given for the products. R. S. C.

Radioactive exchange and adsorption of methyl bromide with several inorganic bromides.—See A., 1944, I, 42.

βββ-Trifluoroethyl iodide. H. Gilman and R. G. Jones (*J. Amer. Chem. Soc.*, 1943, **65**, 2037—2038).—$CF_2{\cdot}CHN_2$ with HI–PhMe at —75° gives *βββ-trifluoroethyl iodide* (I) (77%), b.p. 54·5—55°/730 mm., obtained only in 4—5% yield from $CF_3{\cdot}CH_2{\cdot}OH$ by I–P. With Mg in Et_2O–N_2, (I) gives no Grignard reagent (Michler's ketone test) but instead $CH_2{:}CF_2$, b.p. 91°/740 mm. R. S. C.

Electrolysis of the nitroparaffins. R. Pearson and W. V. Evans (*Trans. Electrochem. Soc.*, 1943, **84**, *Preprint* 21, 227—231).—Electrolysis of $MeNO_2$ containing 1% of NMe_3 between Pt electrodes at 15° with c.d. 0·8—2·4 amp. per dm.^{2} gives at the cathode NHMe·OH (oxalate, m.p. 157—158°; sulphate, m.p. 129°) in 53% yield and at the anode $NO_2{\cdot}[CH_2]_2{\cdot}OH$, b.p. 191·5°, in 25% yield, identified further by reduction to $NH_2{\cdot}[CH_2]_2{\cdot}OH$; NO, NH_2OH, and some $CH_3{\cdot}N{\cdot}OH$ are also obtained. Under similar conditions $EtNO_2$ affords NHEt·OH (oxalate, m.p. 95—96°) in 40% yield and $NO_2{\cdot}[CHMe]_2{\cdot}OH$ in 25% yield with some NH_2OH and apparently CHMe:N·OH. In aq. alkali NH_2OH does not result and the solution contains NO_3^- but not NO_2^-; O_2 is evolved at the anode. $Pr^βNO_2$ and NMe_3 give a green solution probably containing $NO{\cdot}CMe_2{\cdot}NO_2$; on electrolysis $NHPr^β{\cdot}OH$ is formed at the cathode and $COMe_2$ at the anode with a residue of high b.p. In presence of NaOH there is no production of NH_2OH but there is a 15% yield of dinitro-βγ-dimethylbutane which causes partial polarisation of the anode, at which O_2 is evolved. H. W.

Anode reactions in the electrolysis of ethyl alcohol.—See A., 1944, I, 43.

Catalytic dehydrogenation. I. Catalytic conversion of alcohols into aldehydes, paraffins, and olefines. E. J. Badin (*J. Amer. Chem. Soc.*, 1943, **65**, 1809—1813).—Catalytic changes of *n*-$C_xH_{2x+1}{\cdot}OH$ (*x* = 5, 8, 9, 10, and 16) in presence of Raney Ni at 140—275° are reported. Reactions are successively: loosening of an α-H; $R{\cdot}[CH_2]_3{\cdot}OH \rightarrow R{\cdot}[CH_2]_2{\cdot}CHO + H_2$; $R{\cdot}[CH_2]_2{\cdot}CHO \rightarrow CHR{:}CH_2 + CO + H_2$; $CHR{:}CH_2 + H_2 \rightarrow CH_2MeR$; and, slowly, $CO + 3H_2 \rightarrow CH_4 + H_2O$. At 140° only aldehyde is formed. Max. amounts of aldehyde (measured as 2 : 4-dinitrophenylhydrazone; probably present largely as acetal) are obtained at 200—215°, of CH_2MeR at 250°, and of olefine at 275°. Temp. is thus the main factor. n-*Decaldehyde*-2 : 4-*dinitrophenylhydrazone* has m.p. 104°. R. S. C.

Reaction between alcohols and metal oxides. E. Berner (5 *Nordiske Kemikermøde*, 1939, 231—232).—Anhyd. MeOH and CaO give basic Ca methoxide, of very variable composition, which reacts with more MeOH to give $Ca(OMe)_2$ and H_2O. $Sr(OMe)_2$ and $Ba(OMe)_2$ are freely sol. in MeOH at room temp.; their pptn. on heating is due to conversion into an unsolvated modification. PbO and MeOH at room temp. in sunlight or Hg-vapour light give finely-divided Pb; the reaction is quantitatively reversed in darkness. M. H. M. A.

Leaf alcohol. IV. *trans-cis* Problem of the leaf alcohol, Δ^γ-*n*-hexen-α-ol. S. Takei, M. Ono, and K. Sinosaki (*Ber.*, 1940, **73**, [*B*], 950—955; cf. A., 1939, III, 536).—H_2–Pd–$BaSO_4$ converts $CEt{\cdot}C{\cdot}[CH_2]_2{\cdot}OH$ (I) in Et_2O at —18° into *trans*- (II) (96%) (3 : 5-dinitrobenzoate, m.p. 49°; allophanate, m.p. 146°; anthraquinone-2-carboxylate, m.p. 68°) but in xylene at 100° into *cis*-$CHEt{:}CH{\cdot}[CH_2]_2{\cdot}OH$ (III) (3 : 5-*dinitrobenzoate*, m.p. 28°; allophanate, m.p. 143°; anthraquinone-2-carboxylate, m.p. 50°), and in C_6H_6 at 50° into a mixture (cf. Stoll *et al.*, A., 1939, II, 2). Complete hydrogenation in Et_2O yields *n*-$C_6H_{13}{\cdot}OH$ (3 : 5-dinitrobenzoate, m.p. 59—60°). (II) is identical with the natural product (A., 1938, II, 345). (III) is also obtained from Et_2 sorbate by reduction by Na. The dibromide, b.p. 119—122°/6 mm. (4′-*iododi*-

phenylylurethane, m.p. 127°), of (**II**) with KOH–aq. EtOH in the cold gives $C_8H_{19}Br{\cdot}OH$, b.p. 68—69°/3 mm. (*allophanate*, m.p. 171°), and thence at the b.p. (**I**), b.p. 69—71°/16 mm. [*allophanate* (**IV**), m.p. 187°; 3 : 5-*dinitrobenzoate*, m.p. 72°; *anthraquinone-2-carboxylate*, m.p. 129°] (cf. *loc. cit.*), regenerated by distilling (**IV**) + KOH in steam and oxidised by aq. $KMnO_4$ at 70° to $EtCO_2H$.

R. S. C.

Volatile vegetable compounds. XXV. Presence of Matsutake's alcohol (Δ^{α}-*n*-octen-γ-ol) and of 3-methyl*cyclo*hexanol in oil of pennyroyal [*Mentha pulegium*, L.]. Y. R. Naves (*Helv. Chim. Acta*, 1943, **26**, 1992—2001).—Different samples of the oil of Spanish origin which contain piperitenone and *n*-octan-γ-ol also contain octenols. In one such sample *d*-*n*-octan-γ-ol, Δ^{α}-*l*-*n*-octen-γ-ol, and 3-methyl*cyclo*hexanol have been identified; other alcohols are present. dl-n-*Octan-γ-yl allophanate*, m.p. 155·5—156°, appears new. *d*-*n*-Octan-γ-yl allophanate has m.p. 182—182·5°. H. W.

Optically active phytol. P. Karrer, A. Geiger, H. Rentschler, E. Zbinden, and A. Kugler (*Helv. Chim. Acta*, 1943, **26**, 1741—1750).—Partly racemised (+)-citronellol (**I**), b.p. 106—108°/12 mm., $[\alpha]_D^{15}$ +2·9°, is hydrogenated (Pt) to (+)-dihydrocitronellol, b.p. 104—107°/12 mm., $[\alpha]_D^{15}$ +2·56°, which is converted by PBr_3 at 0° into (−)-dihydrocitronellyl bromide, b.p. 98—100°/12 mm. This is condensed with $CHAcNa{\cdot}CO_2Et$ to Et (−)-βζ-dimethyloctylacetoacetate, b.p. 155°/12 mm., ϕ −1·6°, hydrolysed by KOH–MeOH at room temp. to (+)-*hexahydro-ψ-ionone* (**II**), b.p. 122°/12 mm., $[\alpha]_D^{15}$ +0·55°, which is purified to optical homogeneity through the *semicarbazone*, m.p. 95°. (**II**) and C_2H_2 afford γηλ-*trimethyl*-Δ^{α}-*dodecinen-γ-ol*, b.p. 140—142°/13 mm., ϕ +0·82°, converted by partial hydrogenation (Pt or Pd) into γηλ-*trimethyl*-Δ^{α}-*dodecen-γ-ol*, b.p. 142—144°/13 mm., which gives successively γηλ-*trimethyl*-Δ^{β}-*dodecenyl bromide* (which could not be purified), Et γηλ-trimethyl-Δ^{β}-dodecenylacetoacetate, and (−)-ζκξ-*trimethyl*-Δ^{ε}-*pentadecen-β-one* (**III**), b.p. 175—178°/11 mm., ϕ_D −0·20°. Thus far the compounds contain only one asymmetric C but partial reduction of (**III**) involves the formation of a second asymmetric centre. Only one (−)-ζκξ-*trimethylpentadecan-β-one*, b.p. 168—172°/11 mm., ϕ_D −0·24°, appears to be formed as judged by the behaviour of the cryst. *semicarbazone*, m.p. 68°, $[\alpha]_D$ −0·35° in EtOH. Optical homogeneity at $C_{(\zeta)}$ is not regarded as definitely established. Addition of C_nH_2 to the ketone leads to γηλο-*tetramethyl*-Δ^{α}-*hexadecinen-γ-ol*, b.p. 159—164°/0·6 mm., ϕ_D −0·2°, transformed by partial catalytic hydrogenation into (−)-γηλο-*tetramethyl*-Δ^{α}-*hexadecen-γ-ol* [(−)-iso*phytol*], b.p. 136—141°/0·1 mm., ϕ_D −0·2°, transformed by PBr_3 into phytyl bromide, converted by KOAc in $COMe_2$ followed by hydrolysis into (−)-*phytol* (**IV**), b.p. 132°/0·02 mm., ϕ 0·18°. Since the processes involved in the production of (**IV**) are analogous to those used in the isolation of chlorophyll phytol, the optical inactivity of the latter compound is not due to racemisation during isolation. Re-examination of a phytol obtained from stinging nettles has disclosed an optical activity equal in magnitude but opposite in sign to that of (**IV**). The reality of the observation is established by ozonisation of the compound to (+)-ζκξ-trimethylpentadecan-β-one with ϕ +0·22° (synthetic ketone −0·22°). Further the ketone is oxidised (CrO_3) to (+)-γηλ-trimethyltridecoic acid, ϕ +0·2—0·24°. An optically active, dextrorotatory phytol, therefore, is sometimes found in the plant of which (**IV**) may be the optical antipode. Previous observations of optically inactive phytol in plants are due to the natural occurrence of both *d*- and *r*-phytol. H. W.

Vitamin-*A*. P. Karrer and E. Bretscher (*Helv. Chim. Acta*, 1943, **26**, 1758—1778).—The unsaponifiable matter of winter trout-liver oil is largely freed from sterols by freezing and purified by repeated chromatography over $Ca(OH)_2$ followed by distillation in a cathode-ray vac. The best specimens of vitamin-A_2 thus obtained still contain ~2—3% of -*A* as judged by the yield of geronic acid after ozonisation. This result invalidates the formulæ for -A_1 proposed by Gillam *et al.* (A., 1938, III, 315) and by Gray (A., 1942, II, 185). The isolation of $COMe_2$ and CH_2O by the ozonisation of -A_2 indicates that it may be a mixture of isomerides, $CMe_2{:}CH{\cdot}[CH_2]_2{\cdot}[CMe{:}CH{\cdot}CH{:}CH]_2{\cdot}CMe{:}CH{\cdot}CH_2{\cdot}OH$ and $CH_2{:}CMe{\cdot}[CH_2]_2{\cdot}[CMe{:}CH{\cdot}CH{:}CH]_2{\cdot}CMe{:}CH{\cdot}CH_2{\cdot}OH$, similar to that occurring in natural citronellal. It is, however, possible that the production of CH_2O is due to an isomerisation within the mol. under the action of O_3 since -*A* gives the product in smaller amount than -A_2 and nearly equal amounts are derived from carotene and lycopene; in these cases it is undoubtedly due to subsidiary reactions or isomerisations. The constitution of -A_2 is confirmed by its hydrogenation to dihydrophytol, isolated as the allophanate, m.p. 73°. The purest specimens of -A_2 have ~1/10th of the physiological activity of -*A*; this is due in part to the presence of -*A*, but it appears that the rat has a limited capacity to cyclise -A_2 to -*A*. H. W.

Derivatives of α-bromo-β-methyl-*n*-valeric acid. C. D. Hurd and F. W. Cashion (*J. Amer. Chem. Soc.*, 1943, **65**, 2037).—$CHMeEt{\cdot}CH_2{\cdot}CO_2H$ with red P–Br at 95° gives α-*bromo-β-methyl-n-valeryl bromide* (54%), b.p. 98—100°/23 mm., and thence the *amide*, m.p. 104°, *anilide*, m.p. 84°, and p-*toluidide*, m.p. 105°.

R. S. C.

Course of autoxidation reactions in polyisoprenes and allied compounds. VII. Rearrangement of double linkings during autoxidation. E. H. Farmer, H. P. Koch, and D. A. Sutton (*J.C.S.*, 1943, 541—547; cf. A., 1943, II, 151).—Et linolenate (**I**) and Me docosahexaenoate (**II**), both showing unsaturation of the methylene interrupted type, ·C:C·C·C:C·C·C:C·, are shown by spectrographic measurements to develop conjugated-diene and -triene unsaturation during incorporation of mol. O_2. (**II**) is obtained from glycerides of cod-liver oil, which are converted by MeOH–HCl into Me esters, the C_{22} ester fraction is separated by mol. distillation at <115°, and after rapid hydrolysis with KOH–MeOH, the K soaps are converted through the free acid into Li soaps, and the purified, more sol., Li soap yields the free acid and thence (**II**), which is purified by mol. distillation in N_2 or high vac.; the yellow colour developed in O_2 is removed by chromatographic treatment (Al_2O_3) in purified N_2. (**I**) absorbs 1·1% of O_2 in 24 hr., 3·7% in 48 hr., and 12% in 110 hr.; (**II**) absorbs 6·3% in 72 hr., and a second sample, 7·2% in 24 hr. Extent of double linking displacement is correlated with degree of peroxidation. After incorporation of 1 mol. of O_2, rearrangement of double linkings in (**I**) has progressed to a stage at which ~28·5% of ester contains 2 double linkings in conjugation, and 4·5% has 3 conjugated. (**II**) exhibits a similar rearrangement, as shown by the development of intense absorption in the originally feeble absorbing regions of 2340 and 2700 A. (cf. Triebs, A., 1942, II, 392). Squalene (rectified by mol. distillation at <112°, and purified by chromatographic treatment in N_2) and rubber (purified by fractional dissolution of crepe rubber in petroleum–$COMe_2$ in N_2) show another type of unsaturation, ·C:C·C·C:C·C·C·C:C·, and do not develop conjugated units. No representative increase in absorption of light is noted. Such small increases observed in the spectra of squalene or two of its oxidation products are probably due to small degrees of conjugation or to formation of peroxide groups. Apart from an induction period (no O_2 is absorbed in 2 days, but 8·7% is absorbed in 10 days), the result of oxidising (**I**) at room temp. in complete darkness is the same with regard to efficiency of peroxide formation and extent of double linking rearrangement as that observed in summer daylight. Mechanisms of autoxidative reactions are discussed. A. T. P.

Configurative relation between optically active lactic acid and α-hydroxybutyric acid. A. Fredga, M. Tenow, and I. Billstrom (*Arkiv Kemi, Min., Geol.*, 1943, **16**, **A**, No. 21, 10 pp.).—*r*- (**I**), through the brucine salt, gives (−)-α-hydroxybutyric acid (**II**), m.p. 55—55·5°, $[\alpha]_D^{25}$ −2·5° in H_2O, −4·1° in $COMe_2$, +1·7° in AcOH, +6·8° in $CHCl_3$. (**I**)–aq. NaOH–CS_2, then EtBr, afford *ethylcarbothiolon-α-hydroxybutyric acid*, $SEt{\cdot}CS{\cdot}O{\cdot}CHEt{\cdot}CO_2Et$ (**III**), m.p. 58—59°, resolved into the (+)- (**IV**), m.p. 31·5—32° (*cinchonidine salt*, $+H_2O$), and (−)-*acid*, m.p. 30·5—31·5° (*brucine salt*, $+3H_2O$). The (+)-acid, also obtained from (−)-(**I**), shows vals. of $[\alpha]_D^{25}$ +39·2° in C_6H_6, +14·5° in $CHCl_3$, +6° in AcOH, which are similar to those of $SEt{\cdot}CS{\cdot}O{\cdot}CHMe{\cdot}CO_2H$ (**V**). M.p. curves of (+)- and (−)-(**II**) or (**III**), *r*-(**III**) and *r*-(**II**), (+)-(**III**) and (+)-(**V**) (eutectic) are shown. The 1 : 1 mol. compound, indicated from the curve derived from (+)-(**III**) and (−)-(**V**), gives a continuous m.p. curve with *r*-(**V**), but with *r*-(**III**) affords a eutectic. The steric series (**II**), (**IV**), (+)-(**V**), (+)-$OH{\cdot}CHMe{\cdot}CO_2H$ is deduced.

A. T. P.

Irreversible transformation of dehydroascorbic acid.—See A., 1944, III, 127.

Rearrangement of allyl-type esters of β-keto-acids. W. Kimel and A. C. Cope (*J. Amer. Chem. Soc.*, 1943, **65**, 1992—1998).—$CH_2Ac{\cdot}CO{\cdot}O{\cdot}CH_2{\cdot}CH{:}CH_2$ (**I**) and its derivatives at 250° give $Ac{\cdot}[CH_2]_2{\cdot}CH{:}CH_2$ etc. and CO_2, reaction proceeding by chelation, migration of allyl etc. to the CH_2 of $CO{\cdot}CH_2{\cdot}CO$ with inversion, shift of the ethylenic linking, and finally loss of CO_2. Similar reactions with $CH_2Bz{\cdot}CO{\cdot}O{\cdot}CHR{\cdot}CH{:}CHR'$ (R and R' = H or Me) occur even more readily, owing to the superior activating effect of Bz on CH_2. Formation of $Ac{\cdot}[CH_2]_2{\cdot}CH{:}CHPh$ (**II**) or $CH_2Ac{\cdot}CHPh{\cdot}CH{:}CH_2$ (**III**) from $CH_2Ac{\cdot}CO_2Et$ and $CHPh{:}CH{\cdot}CH_2{\cdot}OH$ (Carroll, A., 1941, II, 310) occurs by re-esterification in presence of the alkaline catalyst, followed by an allylic shift of Ph and the ethylenic linking. $CH_2Ac{\cdot}CO_2Me$ and $CH_2{:}CH{\cdot}CH_2{\cdot}OH$ give (**I**) (71%), but the reaction fails with analogous alcohols. The alcohols with diketen and 0·01 mol. of NaOAlk at 0—25° give *β-methylallyl* (**IV**) (85%), b.p. 95—97°/18 mm., *crotyl* (**V**) (83%), b.p. 100—102°/16 mm., Δ^{γ}-*β-butenyl* (**VI**) (89%), b.p. 92—93°/18 mm., *cinnamyl* (**VII**) (69%), b.p. 101—104°/0·025 mm., *α-phenylpropenyl* (**VIII**) (70%), b.p. 77°/0·002 mm., *linalyl* (**IX**) (61%), b.p. 71—74°/0·006 mm., and *geranyl* (**X**) (77%), b.p. 79—80°/0·006 mm., *acetoacetate*. (**X**) contains some neryl ester (disclosing itself by variation of *n*); hydrogenation of (**X**) gives only tetrahydrogeraniol. At the b.p., (**I**) gives $CH_2{:}CH{\cdot}CH_2{\cdot}OH$, $COMe_2$, dehydroacetic acid, and only 5·5% of $COMe{\cdot}[CH_2]_2{\cdot}CH{:}CH_2$ (**XI**), but in Ph_2O at 185—200° gives 31% of (**XI**). In Ph_2O at 200—215° (**IV**) gives *β-methyl*-Δ^{α}-*hexen-ε-one* (26%), b.p. 148—149° (*semicarbazone*, m.p. 136·5—137·5°) (also obtained from $CH_2{:}CMe{\cdot}CH_2Cl$ and $CHAcNa{\cdot}CO_2Et$), (**V**) at 190—220° gives $COMe{\cdot}CH_2{\cdot}CHMe{\cdot}CH{:}CH_2$ (37%), and (**VI**) at 185—200° gives $COMe{\cdot}[CH_2]_2{\cdot}CH{:}CHMe$ (80%), b.p. 151—153° (semicarbazone, m.p. 104·5—105·5° (lit. 97°); with O_3–C_3H_4, and then H_2O_2 gives

MeCHO and COMe·$[CH_2]_2$·CO_2H}. At 250° (**VII**) (no solvent) gives (**III**) (74%), b.p. 85—86°/1 mm. [2 : 4-dinitrophenylhydrazone, m.p. 102—103° (lit., 101—102°)], (**VIII**) at 200—240° gives (**II**) (88%), b.p. 97—99°/0·3 mm. [2 : 4-dinitrophenylhydrazone, m.p. 143·5—145° (lit. 145—146·5°); semicarbazone, m.p. 130·5—131° (lit., 132°)]; geranylacetone, b.p. 101·5—103°/2·5 mm. [semicarbazone, m.p. 94·5—96° (lit. 96°)], is obtained (78%) from (**IX**) at 170—235° or (23%) from (**X**) at 220—230°. $CH_2Bz·CO_2Et$, ROH, and NaOR give *crotyl* (31%), b.p. 112—114°/0·20 mm., and Δ^{γ}-β-*butenyl benzoylacetate* (65%), b.p. 110°/0·5 mm., which at 240—250° give *Ph β-methyl-*Δ^{γ}*-butenyl* (76%), b.p. 98—100°/2·1 mm. (*semicarbazone*, m.p. 176—177·5°; with O_3–C_5H_{12} at −5° and then H_2O–Zn dust–quinol–$AgNO_3$ gives CH_2O and with H_2–Pd–C–EtOH gives COPh·CH_2·CHMeEt), and Δ^{γ}-n-*pentenyl ketone* (83%), m.p. 23°, b.p. 96—97°/9 mm. (*semicarbazone*, m.p. 129—130°; with O_3 gives MeCHO and with H_2–Pd–C gives *n*-C_5H_{13}Ph), respectively. In the pyrolyses yields of CO_2 considerably exceed those of the ketones. R. S. C.

Carboxyphenylhydrazones in the identification of carbonyl compounds. S. Veibel [with A. Blaaberg and H. H. Stevns] (5 *Nordiske Kemikermøde*, 1939, 223—225; cf. A., 1939, II, 133).—*p*-$SO_3H·C_6H_4·NH·NH_2$ is unsuitable for the identification of CO compounds owing to its poor solubility. *o*- (**I**) is as suitable as *p*-$CO_2H·C_6H_4·NH·NH_2$ (**II**) for this purpose; both react normally with α- and γ-CO-acids, but with β-CO-acids (**I**) reacts normally whilst (**II**) yields pyrazolones. (**II**) reacts normally with CH_2Ac_2 whilst (**I**) gives an unidentified substance sol. in acids and pptd. by alkalis. M. H. M. A.

Methanetri-β-propionic acid. V. Prelog and K. Balenovic (*Ber.*, 1940, **73**, [*B*], 875—877).—$CH([CH_2]_2·Br)_3$ is converted by the protracted action of KCN in boiling aq. EtOH into *αε-dicyano-γ-β′-cyanoethylpentane*, m.p. 83°, hydrolysed by boiling aq. H_2SO_4 (1 : 1) to *methanetri-β-propionic acid* [*γ-β′-carboxyethylpentane-αε-dicarboxylic acid*] (**I**), m.p. 108·5—109°. The corresponding Et_3 ester, b.p. 163°/0·06 mm., is condensed by Na in PhMe at 115—120° to *β-4-keto-3-carbethoxy*cyclo*hexylpropionic acid*, m.p. 101°; alkaline hydrolysis affords the free *keto-acid*, decomp. ~80°, which at 100°/0·05 mm. yields β-4-keto*cyclo*hexylpropionic acid, m.p. 69—70° (hydrate, m.p. 55°; 2 : 4-dinitrophenylhydrazone, new m.p. 156°), also obtained by heating (**I**) with Ac_2O (cf. Harris *et al.*, A., 1938, II, 332). H. W.

Hydroxyl-ion-catalysed aldol condensation of benzaldehyde with methyl ethyl ketone and acetone.—See A., 1944, I, 42.

α-Keto-β-hydroxybutyric acid. E. Hoff-Jørgensen (5 *Nordiske Kemikermøde*, 1939, 251—252).—CHMeBr·CO·CN (from EtCO·CN with Br–AcOH) is heated with aq. $Pb(OAc)_4$ for 30 min. at 70°, $PbBr_2$ filtered off and all Pb removed with H_2S, and the solution evaporated 4—5 times, with H_2O addition, at 50° to give n-*α-keto-β-hydroxybutyramide*, m.p. 214°, which is converted via the *Me* ester, liquid, and the *Ba* salt into the corresponding *acid* (**I**). (**I**) reduces Fehling's solution and is decarboxylated at pH >7, but is stable in acid solution. M. H. M. A.

Stabilisation of keto-compounds by acetalisation. M. Kühn (*J. pr. Chem.*, 1940, [ii], **156**, 103—149; cf. Salmi, A., 1938, II, 427).—Stabilisation of CO-compounds as acetals, which because of their tendency to form peroxides may be useful as polymerisation catalysts, is studied. Cyclic acetals are obtained from various CORR′ and a glycol in C_6H_6 or C_2HCl_3 using an acid catalyst (*e.g.*, $PhSO_3H$); the H_2O formed in the reaction is removed by distillation. Thus, saturated α-, β-, γ-, and δ-CO-acids (as esters) all give 5- and 6-membered ring ketals; the ring is completely stable to alkali and is hydrolysed by dil. HCl only at >50°. Reaction does not occur with ketones containing C:C αβ to the CO (*e.g.*, CHR:CAc·CO_2Et; R = Ph, 2-furyl) or with compounds which can enolise to produce C:C·CO· (*e.g.*, $CHAc_2·CO_2Et$; CN·CHPh·COMe). $CEt_2Ac·CO_2Et$ does not react. *cyclo*Hexanone (**I**), glycerol, and a trace of $PhSO_3H$ in boiling C_6H_6 thus give cyclo*hexanone* γ(or β)-*hydroxy-αβ*(or αγ)-*propylene ketal* (64%), b.p. 133—135°/15 mm. [*chloroacetate*, b.p. 170—174°/15 mm., with $NEt_2·[CH_2]_2·OH$ in EtOH affords the 1 : 1 additive *compound*, m.p. 196° (decomp.)], ultra-violet irradiation of which causes strong peroxide formation. $CH_2Cl·[CH_2]_2·OH$ with camphor (in C_6H_6 + $PhSO_3H$) and COPhMe (in PhMe + H_2SO_4) gives the *γ-chloro-αβ-propylene ketals*, b.p. 146°/17 mm. and 138—140°/15 mm., respectively. $(CH_2·OH)_2$ and COPh·CH_2Cl in C_6H_6 + $PhSO_3H$ afford the *ethylene ketal* (95%), b.p. 144—146°/15 mm., m.p. 67°, the Cl of which is stable to EtOH–NaOH and to CHNaAc·CO_2Et or OMe·$[CH_2]_2$·O·$[CH_2]_2$·ONa in PhMe; it slowly forms a Grignard reagent. COPh·$CHCl_2$ does not similarly react but *ethylene ketals* of the following are prepared: COPh·CH_2Br, b.p. 154°/17 mm., m.p. 60—61° (no reaction with MeOH–NaOMe at 0°/10 hr.), COMe·CH_2Br, b.p. 76—78°/16 mm., $CO(CH_2Br)_2$, b.p. 113°/16 mm., COMe·CH_2Cl, b.p. 62—64°/18 mm., and $CO(CH_2Cl)_2$, b.p. 105°/12 mm. CH_2:CH·COMe (**II**), $(CH_2·OH)_2$, and C_6H_6 + $PhSO_3H$ give a mixture of probably $(COMe·[CH_2]_2·O·CH_2)_2$ and its diketal; COMe·$[CH_2]_2$·Cl [from (**II**) and HCl in C_6H_6] gives an impure product [from which the ketal of (**II**) could not be obtained

by treatment with alkali] and COPh·$[CH_2]_2$·Cl affords a polymerisation product. CHPh:CH·COPh and CHR:CH·COMe (R = Ph, 2-furyl) did not react (cf. above). Glucose and (**I**) in C_6H_6–BuOH–$PhSO_3H$ give 1 : 2 : 5 : 6-*di*cyclo*hexylidene*-3 : 4-*anhydroglucofuranose* (**III**) (R = *cyclo*hexylidene), b.p. 193—195°/0·5 mm.; phenylglucosazone similarly affords a *product* containing 80% of the 3 : 4 : 5 : 6-di*cyclo*hexylidene ether. 3 : 4 : 5 : 6-*Di*iso*propylideneglucosazone* (from $COMe_2$ + $PhSO_3H$) is a resin. $NEt_2·[CH_2]_3$·COMe (as hydrochloride which is dried by C_6H_6) does not react with $CH_2R·OH$ (R = Me, Pr, Bu, C_7H_{15}) and H_2SO_4 in various hydrocarbons but gives the *ethylene*, b.p. 116°/15 mm., and γ(or β)-*hydroxy-αβ*(or αγ)-*propylene ketal*, b.p. 163°/15 mm. $NEt_2·[CH_2]_2$·COMe affords the *ethylene*, b.p. 93—94°/13 mm., 208°/760 mm. (the wax-like quaternary *salt* with $C_{12}H_{25}Br$ is an emulsifying agent for oils), αγ-*butylene*, b.p. 112—113°/13 mm., and γ(or β)-*hydroxy-αβ*(or αγ)-*propylene ketal*, b.p. 145—150°/12 mm. Me *β-N-cyclo*hexyl-*N*-ethylaminoethyl ketone (from $C_6H_{11}·NHEt$,HCl, CH_2O, and $COMe_2$) and 2-*N-cyclo*hexyl-*N*-methylaminomethyl*cyclo*hexanone [from (**I**), *cyclo*hexylamine hydrochloride, and CH_2O] give *ethylene ketals*, b.p. 166°/14 mm. and 190—192°/14 mm., respectively. *NN*-Di-(γ-keto-Δ$^{\delta}$-pentenyl)*cyclo*hexylamine [from *cyclo*hexylamine sulphate, (**II**), and $(CH_2O)_p$ in AcOH] does not react with $(CH_2·OH)_2$ in C_6H_6 + $PhSO_3H$; diacetonamine similarly decomposes but diacetone-ethylamine and Me *β-cyclo*hexylaminoethyl ketone [from *cyclo*hexylamine and (**II**)] form *ethylene ketals*, b.p. 84—86°/14 mm. and 162—163°/18 mm., respectively. The *hydroxypropylene ketal* obtained from glycerol and mixed COPh·CH_2·NMe_2RCl (R = C_{10}—C_{20} alkyl) forms a frothy aq. solution which emulsifies oils.

$CH_2Ac·CO_2Et$ (**IV**) does not react with $[CH_2]_4(OH)_2$ or various $CH_2R·OH$ in C_6H_6 + $PhSO_3H$ or PhMe + H_2SO_4; its ethylene ketal (**V**) (*loc. cit.*) is hydrolysed by 5N-aq. EtOH–NaOH to $CH_2Ac·CO_2H$ ethylene ketal (readily sol. in H_2O), which can be esterified to (**V**) (46% yield). The αγ-butylene ketal of (**IV**) is similarly hydrolysed. (**IV**) also yields the γ(or β)-*hydroxy-αβ*(or αγ)-*propylene*, b.p. 145°/14 mm., and *γ-chloro-αβ-propylene ketal* (**VI**), b.p. 132°/13 mm. Boiling MeOH–NaOMe converts (**VI**) into the not quite pure *αβ-allene ketal* (**VII**), b.p. 118—120°/13 mm.; MeOH–NaOPh gives (**VII**) (42%) and the *γ-phenoxy-αβ-propylene ketal* (48%), b.p. 198°/11 mm., and Na *p-iso*octylphenoxide in PhMe affords the γ-p-iso*octylphenoxy-αβ-propylene ketal*. *Et dodecylacetoacetate*, b.p. 168—170°/0·5 mm., gives the *ethylene ketal*, b.p. 184—186°/0·5 mm. (corresponding *acid*, m.p. 63°). *Ethylene ketals* of the following are prepared: $CO(CH_2·CO_2Et)_2$, b.p. 162—164°/25 mm., $CH_2Ph·CHAc·CO_2Et$, b.p. 178—179°/11 mm., Et_2 α-acetylglutarate, b.p. 180—182°/24 mm., Me Et(α) α-acetylglutarate, b.p. 168—170°/15 mm. (*γ-chloro-αβ-propylene ketal*, b.p. 209—210°/17 mm.), Et γ-acetylbutyrate, b.p. 135—136°/17 mm., Et lævulate, b.p. 110—112°/15 mm., $AcCO_2Et$, b.p. 80—81°/15 mm., Et and Bu α-formylphenylacetate, b.p. 172—174°/15 mm. and 212—214°/20 mm., respectively, Et γ-ketobutylmalonate, b.p. 162—164°/14 mm., Et δ-keto-α-cyanohexoate, b.p. 168—170°/14 mm., and Et_2 α-acetylsuccinate, b.p. 162°/14 mm. Et phenacylacetoacetate and $(CH_2·OH)_2$ (2 mols.) in PhMe + $PhSO_3H$ give the *di*(*ethylene ketal*), b.p. 174—178°/0·5 mm., m.p. 62—64° (free *acid*, m.p. 150—151°), and Et 2-phenyl-5-methylfuran-3-carboxylate (free acid, m.p. 179—181°). 2-Chloro*cyclo*hexanone and CHNaAc·CO_2Et in PhMe followed by $(CH_2·OH)_2$–$PhSO_3H$ give *Et* 1-*methyl*-3 : 4 : 5 : 6-*tetrahydrocoumarone*-2-*carboxylate*, b.p. 143—144°/13 mm. (free *acid*, m.p. 161°). $CH_2(CHAc·CO_2Et)_2$ affords the *di*(*ethylene ketal*), b.p. 214—218°/20 mm. H. B.

Deuterium as indicator in keto–enolic tautomerism. A. Tananger (5 *Nordiske Kemikermøde*, 1939, 229—230).—The type of di-enolisation in diketo-compounds is studied by introducing D into an active CH_2 group and measuring the rate of enolisation and the distribution of D in the dienol. M. H. M. A.

Behaviour of trimethylamine, trimethylammino-sulphur trioxide, and trimethylamine oxide towards sulphur dioxide.—See A., 1944, I, 16.

Additive compounds of trimethylamine with boron fluoride and its methyl derivatives.—See A., 1944, I, 44.

Interaction of higher α-chloroparaffins with ammonia, primary, *sec.*, and *tert.* amines. O. Westphal and D. Jerchel (*Ber.*, 1940, **73**, [*B*], 1002—1011).—RCl (R = *n*-alkyl here and below) with 1 : 1 liquid NH_3–EtOH give mainly NHR_2 with smaller amounts of NH_2R and NR_3; the amount of NR_3 decreases with the size of R. Thus, *n*-$C_8H_{17}Cl$ (**I**) at 140° gives *n*-$C_8H_{17}·NH_2$ (11·4%), b.p. 76—78°/12 mm., (*n*-$C_8H_{17})_2NH$ (~40%), m.p. 35°, b.p. 142—147°/3 mm., and *tri-n-octylamine* (~22%), b.p. 183—185·5°/3 mm. *n*-$C_{12}H_{25}Cl$ (**II**) at 170° gives (*n*-$C_{12}H_{25})_2NH$ (**III**) (81%), m.p. 57—58° (lit. 55—56°) [hydrochloride, dimorphic (transition point ~72°), m.p. ~200° (decomp.)], but at 110° gives *n*-$C_{12}H_{25}·NH_2$ (**IV**) (16%) [*hydrochloride*, m.p. 183—186° (decomp.)] and (**III**) (64%). H_2–Ni–Co–Cu at 100°/~100 atm. reduces *n*-$C_{11}H_{23}$·CN in MeOH–H_2O (150 : 80 ml.) to (**IV**) but in 96% EtOH to (**III**). *n*-$C_{16}H_{33}Cl$ (**V**) at 170° gives

much (n-$C_{16}H_{33})_2NH$ and 24% of n-$C_{16}H_{33}$·NH_2 (*hydrochloride*, m.p. 178°). In EtOH at 175° (**II**) and (**IV**) give 47% of pure (**III**). With NH_2Me in a little EtOH, RCl gives NHMeR and $NMeR_2$ (only with lower alkyl), but, if R = $C_{\leq 6}$, no $NMeR_2Cl$. Thus, $Bu^{\alpha}Cl$ at 100—110° gives *methyldi*-n-*butylamine* (69%), b.p. 53·5—54°/11 mm., and some $NHMeBu^{\alpha}$. n-$C_6H_{13}Cl$ at 100° gives much NHMe·C_6H_{13}-n and 40% of $(n\text{-}C_6H_{13})_2NMe$, b.p. 118°/12 mm. At 140° (**I**) gives n-C_8H_{17}·NHMe (24%) and *methyldi*-n-*octylamine* (30%), b.p. 143—145°/3 mm. At 160° (**II**) gives n-$C_{12}H_{25}$·NHMe (**VI**) (59%), b.p. 108—110°/1·5 mm. (*hydrochloride*, m.p. 181—184°), and *methyldi*-n-*dodecylamine* (37%), m.p. 15—16°, b.p. 201°/1·5 mm. [obtained in 51% yield from (**II**) and (**VI**) in EtOH at 160°]. At 140—150° (**V**) gives n-$C_{16}H_{33}$·NHMe (15%) (*hydrochloride*, m.p. 169—170°) and $(n\text{-}C_{16}H_{33})_2NMe$ (68%), m.p. 36—37° (lit. 34—35°), b.p. 269—271°/1 mm. With *sec.* amines RCl in MeOH or EtOH (not C_6H_6 or light petroleum) gives, usually, good yields of *tert.* base. *E.g.*, $NHEt_2$ with (**I**) at 160° gives *diethyl*-n-*octylamine*, b.p. 112—113°/12 mm., and with (**II**) at 140° gives *diethyl*-n-*dodecylamine* (86%; in absence of EtOH), b.p. 122—124°/2 mm. (*hydrochloride*, m.p. 119·5°). $NH(CH_2Ph)_2$ and (**II**) at 150° give *dibenzyl*-n-*dodcecylamine* (75%), b.p. 219—220°/2 mm. (hydrochloride, m.p. 101°). $NHMe_3$ and (**V**) at 140° give *dimethyl*-n-*hexadecylamine* (82·5%), b.p. 138°/1 mm. (hydrochloride, m.p. 198°). Higher alkyl chlorides and *tert.* amines react with difficulty in EtOH and not at all in other solvents or alone. NMe_2·CH_2Ph (**VI**) and (**I**) in a little EtOH at 105° (24 hr.) give *benzyldimethyl*-n-*octylammonium chloride* (~90%), f.p. ~0°. NMe_3 and (**II**)–EtOH at 80—90° give *trimethyl*-n-*dodecylammonium chloride* (75—80%), m.p. ~37°. (**VI**) and (**II**)–EtOH at 90° (45 hr.) give *benzyldimethyl*-n-*dodecylammonium chloride* (~100%), an oil. NMe_3 and (**II**)–EtOH at 180° (18 hr.) give n-$C_{12}H_{25}$·NMe_2 (*hydrochloride*, m.p. ~132°). NMe_3 and (**V**)–EtOH at 100—105° (12—16 hr.) give n-$C_{16}H_{33}$·NMe_3Cl, m.p. ~70° (lit. 240°). (**VI**) and (**V**)–EtOH at 90° (28 hr.) give *benzyldimethyl*-n-*hexadecylammonium chloride* (70%), m.p. 58°. R. S. C.

Constitution of thionylamines. K. A. Jensen (5 *Nordiske Kemikermøde*, 1939, 216—217).—The absence of *syn*- and *anti*-forms and their low dipole moments support the resonance structure: R–N=S→O ⇌ R–N←S=O. M. H. M. A.

Reaction of *d*-glucosamine with *o*-phenylenediamine. R. Lohmar and K. P. Link (*J. Biol. Chem.*, 1943, **150**, 351—352).—*d*-Glucosaminic acid and o-$C_6H_4(NH_2)_2$ (**I**) do not give a cryst. product. Direct oxidative condensation of *d*-glucosamine hydrochloride with (**I**) in presence of $Cu(OAc)_2$–aq. AcOH at 50° affords 3-(*D-arabo*-tetrahydroxybutyl)quinoxaline, m.p. 192—193° (decomp.), $[\alpha]^{20}$ −85·8° in 4N-HCl (tetra-acetate, m.p. 121°, $[\alpha]_D^{20}$ −29·2° in $CHCl_3$) (cf. Ohle, A., 1934, 392). A. T. P.

Amino-acids and peptides. XV. Physical properties of *l*(+)- and *d*(−)-alanine. M. S. Dunn, M. P. Stoddard, L. B. Rubin, and R. C. Bovic (*J. Biol. Chem.*, 1943, **151**, 241—258).—Benzoyl-*dl*-alanine is resolved into its optical components by successive use of strychnine and brucine in aq. solution and the optically active substances are hydrolysed by HCl. The following sp. rotations are recorded: *l*-strychnine benzoyl-*l*(+)-alanine dihydrate, $[\alpha]_D$ −10·45° in H_2O; *l*-brucine benzoyl-*d*(−)-alanine (+4·5H_2O), $[\alpha]_D$ −26·53° in H_2O; benzoyl-*l*(+)-alanine, $[\alpha]_D$ +33·4 in N-NaOH; benzoyl-*d*(−)-alanine, −32·5° in 1·05N-NaOH; *l*(+)-alanine (**I**), $[\alpha]^{25}$° +13·77° ±0·02° in 6·0N-HCl; *d*(−)-alanine (**II**), $[\alpha]_D^{25}$ −13·60° ±0·01° in 6N-HCl. Vals. of $[\alpha]_D^{\theta}$ (θ varied between 0·50° and 45·0°) (**I**) and (**II**) in 7·25N-, 5·97N- (c = 10, 6, or 3·5), 4·83N- (c = 2), 0·884N- (c = 8), 0·502N- (c = 4·5), and 0·228N-HCl (c = 2), and in H_2O (c = 10 or 6) are recorded. The solubilities of (**I**) and (**II**) in H_2O have been determined. The sp. rotations of (**I**) and (**II**) recorded in the literature have been evaluated by means of temp. and solute concn. factors derived from the present authors' data. H. W.

Dihydroxyacyl derivatives of β-alanine and *l*-leucine from tunny fish liver —See A., 1944, III, 124.

Isolation of valylvaline from gramicidin hydrolysates. H. N. Christensen (*J. Biol. Chem.*, 1943, **151**, 319—324).—Valylvaline (**I**) has been isolated as the *Bz* derivative (**II**), m.p. 218°, apparently optically inactive, from hydrolysates of gramicidin (**III**) prepared by boiling this substance with 16% HCl for 6 or 24 hr. (none obtained in 2 hr.). The resulting mixture of NH_2-acids is fractionated as the Cu salts and the fraction sol. both in H_2O and in MeOH is freed from reagents and benzoylated. When completely hydrolysed (**II**) yields BzOH and 2 mols. of *dl*-valine, identified as the Ac (**IV**), m.p. 149°, and p-*toluenesulphonyl* (**V**), m.p. 170° (corr.), derivatives. In separate experiments ~90% of the N was recovered as valine hydrochloride, 80% as (**IV**), and 50% as (**V**). The implication of the presence of (**I**) in the hydrolysates of (**III**) is discussed. H. W.

Amide metabolism in etiolated seedlings. I. H. B. Vickery and G. W. Pucher (*J. Biol. Chem.*, 1943, **150**, 197—207).—See A., 1944, III, 83). Almost quant. results are obtained in Schiff's method for the prep. of aspartic acid (A., 1885, 377) if the asparagine is hydrolysed with HCl (2 mols.) for 3 hr., aq. NH_3 (1 mol.) added, followed by EtOH, and the pH then adjusted to 3·0.

Carbamic acid peptides. New type of peptide. Possible source of ammonia from proteins. A. H. Corwin and (Miss) C. I. Damerel (*J. Amer. Chem. Soc.*, 1943, **65**, 1974—1984).—NH_2·CH_2·CO_2·CH_2Ph,HCl, KCNO, and a slight excess of NaOH in H_2O at 100° (2—3 min.) give N-*carbamylglycine* CH_2Ph ester (50%), m.p. 124·5—126°, converted by CH_2Cl·COCl in boiling C_6H_6 (1 hr.) into N-N′-*chloroacetylcarbamylglycine* CH_2Ph ester (70%), m.p. 179·5—180°, which with H_2–Pd–C in MeOH–H_2O–AcOH (a little) gives N-N′-*chloroacetylcarbamylglycine* (65%), m.p. 198—200° (decomp.), also obtained (56%) from NH_2·CO·NH·CH_2·CO_2H (**I**) by CH_2Cl·COCl in dioxan (not various other solvents). The *Et* ester, m.p. 145—146°, is also prepared. NH_2·CO·NH·CHR·CO_2H and the appropriate acid halide lead similarly to N-N′-*chloroacetylcarbamyl*-dl-*alanine* (51%), m.p. 181—181·5° (decomp.), N-N′-α-*chloropropionylcarbamyl*-*glycine* (51%). m.p. 208·5—211° (decomp.). -dl-*alanine* (56%), m.p. 191—192·5° (decomp.), and -l-*leucine* (46%), m.p. 147—148° (remelts at 148—148·5°), N-N′-α-*bromopropionyl*- (10%), m.p. 201—204° (decomp.), and N-N′-*acetyl*-*carbamylglycine* (poor yield), m.p. 234—235° (decomp.). The halogenated products with liquid NH_3 in ice–$COMe_2$ give N-N′-*glycylcarbamyl*-*glycine* (**II**) (70%), m.p. 192·5—194°, and -dl-*alanine* (**III**) (77%), and N-N′-*alanylcarbamylglycine* (**IV**) (55%), +H_2O (absorbed from air), softens 180°, m.p. 190—195° (decomp.). (**II**)—(**IV**) are amphoteric, having pK_1 ~3·34 and pK_2 ~7·6, and changes in titration curves due to CH_2O resemble those of NH_2-acids and polypeptides. The course of hydrolysis is elucidated by titration. In 0·3N-NaOH at room temp. (**II**) or (**III**) gives glycine + (**I**) or NH_2·CO·NH·CHMe·CO_2H, respectively, (**IV**) gives alanine + (**I**), and NHAc·CO·NH·CH_2·CO_2H gives AcOH + (**I**); to a slight extent, more with (**IV**) than with (**III**), decomp. occurs into NH_2·CHR·CO·NH_2 + CO_2H·NHR′·CO_2H, the amide then decomp. further with liberation of NH_3. In strong alkali, quant. yields of CO_2 and NH_3 are obtained. In 0·3N-HCl at 90—100° (**II**), (**III**), and (**IV**) give NH_2·CHR·CO_2H + NH_2·CO·NH·CHR′·CO_2H, with subsequent ring-closure of the latter product to hydantoin (**V**) or methylhydantoin (**VI**), respectively; ring-closure to (**V**) is slower than that to (**VI**) and only the latter reaction is completed under the conditions of hydrolysis. In H_2O at 90—100° NH_2·CHR·CO·NH·CO·NH·CHR′·CO_2H gives (**V**) or (**VI**) and NH_2·CHR′·CO_2H; thus (**V**) is isolated from (**II**), alanine from (**III**), and glycine and (**VI**) from (**IV**). NHAc·CO·NH·CH_2·CO_2H gives, slowly, AcOH + (**I**). In boiling 5N-HCl, (**II**) gives CO_2 (16·3%) and NH_3; thus, if ·NH·CO· units occur in polypeptides, some CO_2 and NH_3 may be formed on hydrolysis but the amount of ·NH·CO· cannot be calc. by simple stoicheiometric rules. R. S. C.

Crystalline quinine salt of pantothenic acid. Synthesis and resolution of the racemate. R. Kuhn and T. Wieland (*Ber.*, 1940, **73**, [*B*], 971—975).—COCl·$[CH_2]_2$·NH_2,HCl (prep. from the acid by PCl_5–AcCl) with CH_2Ph·OH at 70—80° give β-alanine CH_2Ph ester hydrochloride, m.p. 100—101° [derived *platinichloride*, m.p. 202—203° (block)], which with the lactone (**I**) of OH·CH_2·CMe_2·CH(OH)·CO_2H (**II**) at 100°, and then H_2–PtO_2 in AcOH or HCO_2H, gives syrupy *dl*-pantothenic acid, obtained pure by adsorption from H_2O at pH 8·5 on Al_2O_3 and elution by $Ba(OH)_2$. This acid has 2 × 10^7 Sbm units per g. (cf. A., 1943, III, 124). The derived Ba salt (pH 8·5) with quinine sulphate in H_2O gives *l*-pantothenic acid, $[\alpha]_D^{21}$ −26·7° in H_2O, $[\alpha]_D^{24}$ −56·3° in MeOH {Ba, $[\alpha]_D^{24}$ −20·4° in H_2O, and *quinine* salt, m.p. 165—167° (block), $[\alpha]_D^{24}$ −115° in H_2O}, having 4·5—5 × 10^7 Sbm units per g. and a rat dose ~15 μg. per day. With hot, aq. $Ba(OH)_2$, (**I**) gives the derived Ba salt, m.p. 220°, and thence, by quinine sulphate, the quinine salts, m.p. 182—183°, and 164—165°, of (−)- and (+)-(**II**), respectively, and thence *d*-, m.p. 82—84°, $[\alpha]_D^{20}$ +28·0°, and *l*-(**I**), m.p. 76—80°, respectively. R. S. C.

Solubilities of amides etc.—See A., 1944, II, 34.

Structure and insecticidal properties of organic compounds. N. N. Melnikov, N. D. Suchareva, and M. L. Fedder (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **31**, 610—613).—See A., 1944, III, 133. The following are described (% yields in parentheses): Pr^{α} (88), b.p. 108—110°/4 mm.; *allyl* (60), b.p. 115—117°/5 mm.; Bu^{α} (88), b.p. 114—115°/3 mm.; Bu^{β} (92), b.p. 111—113°/4 mm., and *octyl thiocyanate* (63), b.p. 185—187°/16 mm.; Pr^{α} (80), b.p. 125—127°/8 mm., *allyl* (72·5), b.p. 113—114°/5 mm., Bu^{α} (75), b.p. 137—140°/10 mm., Bu^{β} (70), b.p. 125—126°/9 mm., and *octyl* α-*thiocyanobutyrate* (53), b.p. 159—162°/5 mm. J. N. A.

Theory of allyl isomerisation. IV. Allyl thiocyanate → allylthiocarbimide. O. Mumm and H. Richter (*Ber.*, 1940, **73**, [*B*], 843—860; cf. A., 1939, II, 113, 478).—Further evidence is adduced in favour of the view that there is a change in position of attachment of the allyl group in all cases of allyl isomerisation in which the intermediate production of a 6-membered ring is possible even by participation of partial valencies. Technical CHMe:CH·CHO is reduced [Al(OPr$^{\beta}$)$_3$] to CHMe:CH·CH_2·OH, converted by saturated aq. HBr at 0° into a mixture of 87% of the primary and 13% of the *sec.* bromide. Gradual addition of NH_4CNS to this material in well-cooled EtOH leads to *crotyl thiocyanate* (**I**), b.p. 40°/0·7 mm., which can be kept for a few days in the dark at 0° but soon becomes

isomerised at room temp. The presence of the identical chain in (I) and the initial material is proved by ozonisation of (I) and decomp. of the ozonide by H_2O to MeCHO, further identified by oxidation to AcOH in 77% yield [anhyd. NaOAc has m.p. 330° (corr.; block)]. Distillation under atm. pressure causes isomerisation of (I) to crotylthiocarbimide (II), b.p. 158—159°/760 mm., 50°/11·5 mm. (II) is converted by aq. NH_3 into crotylthiocarbamide, m.p. 107—108°, reduced (H_2 at room temp./15 atm., Pd–$BaSO_4$–H_2O) to *sec.*-butylthiocarbamide (III), m.p. 131—133°. Authentic material is obtained as follows: CHMeEtBr is converted by *o*-$C_6H_4(CO)_2NK$ at 210° into sec.-*butylphthalimide* (IV), m.p. 24·5—25·5°, transformed by aq. NaOH at 100° into sec.-*butylphthalamic acid* (V), m.p. 132—133°, and further hydrolysed to CHMeEt·NH_2 [platinichloride, m.p. 228° (decomp.)]. The base is transformed by CS_2 in Et_2O into the *dithiocarbamate*, which with aq. $HgCl_2$ yields successively *sec.*-butylthiocarbimide, m.p. 159·5°, and (III), (II) and *o*-$C_6H_4(CO_2H)_2$ at 155° afford *crotylphthalimide* (*α-methylallylphthalimide*), m.p. 87—88°, and its unsymmetrical *isomeride*, $CO<^{C_6H_4}_{\ \ O}>C{:}N\cdot CHMe\cdot CH{:}CH_2$ (VI), m.p. 52—53°, the former of which is hydrogenated to (IV), further identified by conversion into (V). (VI) is hydrogenated (Pd–$BaSO_4$ in EtOAc) and then partly hydrolysed to sec.-*butyliso*-*phthalamic acid*, $CO_2H\cdot C_6H_4\cdot C(OH){:}N\cdot CHMeEt$, m.p. 101°. (II) is therefore identical with the product described by Charon (A., 1899, i, 848). The product described by Schimmel & Co. (A., 1910, i, 759) is $CHMe{:}CH\cdot CH_2\cdot NCS$. $OH\cdot CHEt\cdot CH{:}CH_2$ is converted into a mixture separated by fractional distillation into γ- and α-ethylallyl chloride. The former compound is slowly transformed by NH_4CNS in well-cooled EtOH into *γ-ethylallyl thiocyanate* (VII), b.p. 55°/1·6 mm., which becomes isomerised with separation of S in a few days at room temp. Fission of (VII) by O_3 gives EtCHO (*p*-nitrophenylhydrazone, m.p. 123—124°) and oxidative fission of the ozonide by alkaline $KMnO_4$ gives $EtCO_2H$ in nearly quant. amount. Distillation under atm. pressure isomerises (VII) to *α-ethylallylthiocarbimide*, b.p. 71°/19 mm., transformed by NH_3 in EtOH at room temp. into *α-ethylallylthiocarbamide*, m.p. 92°; this is reduced to γ-amylthiocarbamide, m.p. 78—79°. γ-Ethylallyl thiocyanate is converted similarly into the corresponding *-carbimide*, b.p. 186—188°. H. W.

Effect of molecular environment on absorption of organic compounds in solution. Compounds containing the chromophore :C·C·C:N·.—See A., 1944, I, 28.

II.—SUGARS AND GLUCOSIDES.

***d*-Ribose. Preparation of a crystalline anhydroribose.** H. Bredereck, M. Köthnig, and (Miss) E. Berger (*Ber.*, 1940, **73**, [*B*], 956–962).—$[\alpha]_D^9$ of *d*-ribose (I) (prep. described) in C_5H_5N at 20° changes regularly from −38·4° (after 4 min.) to −43·1° in 2 days, but const. vals. for *k* are not obtained (cf. Phelps *et al.*, A., 1934, 494). With CPh_3Cl in C_5H_5N at 37° (4 days) and then 100° (0·5 hr.), (I) gives the 5-*CPh*$_3$ *ether* (+0·5EtOH), m.p. 125°, $[\alpha]_D^3$ (in C_5H_5N) + 12·1° (4 min.) → 9·9° (12 hr.) (k = ~0·0205, const.) (reduces Fehling's solution; blue colour with $CuSO_4$–alkali), and thence (Ac_2O–C_5H_5N; room temp.) the 5-*CPh*$_3$ *ether* 1 : 2 : 3-*triacetate*, a syrup, $[\alpha]_D^9$ +4·9° to +5·2° in EtOH, which with HBr–AcOH at 0° gives *anhydroribose* <1, 5> <1, 4> 2 : 3-*diacetate*, m.p. 169°, and thence *anhydroribose* <1, 5> <1, 4>, sinters 225°, m.p. 229—230°, $[\alpha]_D^{20}$ +78·8° to +77·8° in H_2O (reduces Fehling's solution only after hydrolysis; blue colour with $CuSO_4$–alkali). R. S. C.

Carbohydrate characterisation. IV. Identification of *d*-ribose, *l*-fucose, and *d*-digitoxose as benziminazole derivatives. R. J. Dimler and K. P. Link (*J. Biol. Chem.*, 1943, **150**, 345—349; cf. A., 1942, II, 248).—*d*-Ribose and *l*-fucose are oxidised by KOI–MeOH to *d*-ribonic acid (I) (through the K salt) and *l*-fuconic acid (through the Ba salt), and condensation with *o*-$C_6H_4(NH_2)_2$–HCl–H_3PO_4 at 135° then gives d-*ribo*- (II), m.p. 190°, $[\alpha]_D^{25}$ +22·5° in N-HCl (*hydrochloride*, m.p. 196—198°; *picrate*, m.p. 185—186°) (cf. Richtmeyer *et al.*, A., 1942, II, 395), and l-*fuco*-*benziminazole*, m.p. 248—249°, $[\alpha]_D^{26}$ −41·2° in N-HCl [*hydrochloride*, m.p. 224—225°; *picrate*, m.p. 189—191° (also +H_2O)], respectively. K *d*-arabonate (~5%) is also formed during prep. of (I), by epimerisation, and gives insol. d-*arabobenziminazole*, m.p. 235—237°, $[\alpha]_D^{25}$ −45° in N-HCl (*picrate*, m.p. 155—156°), which is not isolated if (I) is prepared by oxidation by the Br–$Ba(OBz)_2$ method of Hudson *et al.* (A., 1929, 1043). Oxidative condensation of *d*-digitoxose in presence of $Cu(OAc)_2$,H_2O-aq. AcOH at 53° for 14 hr. yields d-*digitoxobenziminazole*, m.p. 207—209°, $[\alpha]_D^{25}$ −45·7° (hydrochloride, an oil; *picrate*, m.p. 124—127°). A. T. P.

Reaction of glucose with some amines. A. E. Mitts (*Iowa State Coll. J. Sci.*, 1943, **18**, 68—70).—NH_2R with glucose yields *glucosyl*-n-*butyl*-, m.p. 96—97°, $[\alpha]_D^{25}$ −22° to −7·8° in EtOH, *-amyl*-, m.p. 96—97°, $[\alpha]^{25}$ −22° to −8° in EtOH, *-heptyl*-, m.p. 97—98°, $[\alpha]_D^{25}$ 13° to −7° in EtOH, and *-dicyclohexyl-amine*, m.p. 97—98°, $[\alpha]_D^{25}$ −23·5° to −11·6° in EtOH. Cryst. compounds were not obtained from β-$C_8H_{17}\cdot NH_2$, $NH_2\cdot CHMe\cdot CH_2\cdot NH_2$ and NH_2Pr^{β}. Also prepared were *glucosyl*-n-*octa*-, m.p. 104—105°, and *-hexa-decylamine*, m.p. 106—107°, and *diglucosylethylenediamine*, m.p. 152—153°, $[\alpha]_D$ −17° to +14·5° in EtOH. Hydrogenation (Raney Ni) of these yields N-*butyl*-, m.p. 126—127°, $[\alpha]_D^{25}$ −14° in 50% EtOH, N-*amyl*-, m.p. 129—130°, $[\alpha]_D^{26}$ −138° in 50% EtOH, N-*heptyl*-, m.p. 126—127°, $[\alpha]_D^{25}$ −14° in 50% EtOH, N-cyclo*hexyl*-, m.p. 145—146°, $[\alpha]_D^{25}$ −11° in 50% EtOH, N-*hexadecyl*-, m.p. 123—124°, and N-*octadecyl*-*d*-*glucamine*, m.p. 118—119°, and NN'-*ethylenediglucamine*, m.p. 136—137°, $[\alpha]_D^{25}$ −15·5° in 50% EtOH. F. R. G.

***d*-Fructopyranose, a sugar unfermentable by yeast.** A. Gottschalk (*Austral. J. Exp. Biol.*, 1943, **21**, 133—137; cf. Hopkins *et al.*, A., 1935, 1538).—At 0° and pH 4·3 the rate of fermentation of the β-pyranose form of *d*-fructose by suspension of baker's yeast is minute compared with that of α-*d*-glucose, is independent of the concn. of the yeast, and depends on the partial conversion of *d*-fructopyranose into *d*-fructofuranose. Hence it is the latter alone which undergoes alcoholic fermentation. At 0° and pH 3·05—5·35 the rate of mutarotation of α-*d*-glucose is < one tenth of that of β-*d*-fructopyranose: this indicates that α-*d*-glucose is fermented without first undergoing a change in mol. structure. The pH of the yeast cell is 5·9: its buffering power, which is high compared with that of serum, is chiefly due to its content of salts. W. McC.

Proportion of fructofuranose in *d*-fructose solution at equilibrium. A. Gottschalk (*Austral. J. Exp. Biol.*, 1943, **21**, 139—140).—Advantage is taken of the fact that the only fermentable component of *d*-fructose solution at equilibrium is fructofuranose, to determine the proportion of this form in the equilibrium mixture at pH 4·3. The val. is ~12% at 0° and probably 20% at 20°. W. McC.

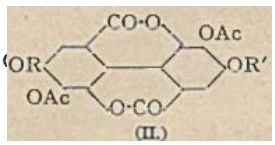
Alkaline degradation of phenyl-β-lactoside, -β-cellobioside, and -*D*-gluco-β-*D*-guloheptoside. (Miss) E. M. Montgomery, N. K. Richtmyer, and C. S. Hudson (*J. Amer. Chem. Soc.*, 1943, **65**, 1848—1854).—Phenyl-β-lactoside in boiling 2·6N-KOH ([α] −36·0° becomes −44·0°) gives, after acetylation (Ac_2O–C_5H_5N), 4-β-*D*-galactopyranosido-*D*-glucosan <1, 5>β<1, 6> hexa-acetate, m.p. 206—208°, [α] −40·8° in $CHCl_3$ (cf. Karrer *et al.*, A., 1933, 1146), converted by Ba(OMe)$_2$ into the unesterified *glucosan*, +H_2O, m.p. 128—130°, [α] −50·6° in H_2O, and anhyd., m.p. 140—144°, [α] −53·5° in H_2O (lit., an oil; does not reduce Fehling's solution), which in 2 : 1 Ac_2O–AcOH containing 2·5% (vol.) H_2SO_4 at 20° gives α-lactose octa-acetate (83%). Phenyl-β-cellobioside hepta-acetate (prep. described), m.p. 206—208° (lit. 193°), [α] −36·0° in $CHCl_3$, with Ba(OMe)$_2$ gives *phenyl-β-cellobioside*, m.p. 211—213°, [α] −59·5° in H_2O, which in 2·6N-KOH at 110—115° gives 4-β-*D*-gluco-pyranosido-*D*-glucosan <1, 5>β<1, 6>, m.p. 122°, [α] −75·0° in H_2O (*loc. cit.*), by way of the hexa-acetate, m.p. 145—146°, [α] −54·4° in $CHCl_3$. *D*-Gluco-β-*D*-guloheptose hexa-acetate, m.p. 134—135°, [α] +4·8° in $CHCl_3$, with HBr–AcOH at room temp. (dark) gives acetobromo-*D*-gluco-α-*D*-guloheptose (I), m.p. 111°, [α] +187° in $CHCl_3$ (cf. lit.). With PhOH and Ag_2CO_3 in C_6H_6 and then Ba(OMe)$_2$ this gives phenyl-*D*-gluco-β-*D*-guloheptoside, m.p. 168°, [α] −90·0° in H_2O (hepta-acetate, m.p. 99°, [α] +8·0° in $CHCl_3$), which in boiling 2·6N-KOH gives D-*gluco*-D-*guloheptosan* <1, 5>β<1, 6> (II), m.p. 95°, [α] +52·9° in H_2O (additive *compound* with 1 NaCl, m.p. 165—167°, [α] +48·6° in H_2O), isolated as *tetra-benzoate*, m.p. 154—155°, [α] +144·4° in $CHCl_3$, or -p-*nitrobenzoate*, m.p. 268°, [α] +218° in C_5H_5N, and converted by H_2SO_4–Ac_2O–AcOH into *D*-gluco-β- (60%) and -α-*D*-guloheptose (20%). 2·02 $NaIO_4$ are consumed by (II) with formation of 0·98 HCO_2H. In C_5H_5N, (II) gives its 2 : 3 : 7-*tri*-p-*toluenesulphonate* (III) (76%), m.p. 157°, [α] +34·6° in $CHCl_3$, and thence the 4-*acetate* 2 : 3 : 7-*tri*-p-*toluenesulphonate*, +$COMe_2$, m.p. 105° (gas), [α] +55·2° in $CHCl_3$, which with NaI in $(CH_2Ac)_2$ at 70° gives the 7-*iodide* 4-*acetate* 2 : 3-*di*-p-*toluenesulphonate* (83%), m.p. 135°, [α] −4·0° in $CHCl_3$. With Ba(OMe)$_2$ at room temp. this gives 4 : 7-*anhydro*-D-*gluco*-D-*guloheptosan* <1, 5>β<1, 6> 2 : 3-*di*-p-*toluenesulphonate* (85%), m.p. 180—182°, [α] −37·0° in $CHCl_3$, also obtained from (III) by NaI directly.

[(Miss) O. P. Hartley.] Methyl-*D*-gluco-β-*D*-guloheptoside, m.p. 167—169°, [α] −74·7° in H_2O, gives its penta-acetate, m.p. 153—154° (lit. 150°), [α] −21·3° in $CHCl_3$ (lit., −16°), also obtained from (I) by MeOH–Ag_2CO_3. Methyl-*D*-gluco-α-*D*-guloheptoside, +0·5EtOAc, hygroscopic, [α] (solvent-free) +111·3° in H_2O (penta-acetate, m.p. 174—175°, [α] +105·5° in $CHCl_3$), and *Cd* D-*gluco*-D-*idoheptonate* [d-β-*glucoheptonate*], +$CdBr_2$ + H_2O, discolours at 190°, [α] −5·7° in H_2O, are reported. [α] are $[\alpha]_D^{20}$. R. S. C.

Synthesis of the acetyl derivative of primulaveroside, the glucoside of the ordinary primrose (*Primula officinalis*). F. Mauthner (*J. pr. Chem.*, 1940, [ii], **156**, 150—153).—Gentisic acid (prep. from *o*-$OH\cdot C_6H_4\cdot CO_2H$ by $K_2S_2O_8$ in aq. NaOH + $FeSO_4$ at room temp.) is methylated (Me_2SO_4, aq. NaOH) to the 5-Me ether, the Me ester, b.p. 261—262° (lit. 235—240°) (prep. by MeOH–HCl), of which with acetobromoprimverose and dry Ag_2O in quinoline gives primulaveroside hexa-acetate, m.p. 198—199°. H. B.

New hamameli-tannin. C. P. Edwards and M. Nierenstein (*Pharm. J.*, 1943, **151**, 241).—The bark of English witch-hazel

(*Hamamelis virginica*, Lin.), extracted with CCl_4 and then $CHCl_3$, yields to cold H_2O *γ-hamameli-tannin* (**I**), m.p. 217—233° (slight decomp.), and then to hot H_2O ellagitannin, m.p. 347° (decomp.), $[\alpha]_D^{11}$ +23·07° in H_2O, $[\alpha]_D^{19}$ +17·11° in EtOH. (**I**) is 3 : 4 : 5 : 1-$(OH)_3C_6H_2{\cdot}CO_2{\cdot}[C_6H_{10}O_4{\cdot}O]_2{\cdot}CO{\cdot}C_6H_2(OH)_2{\cdot}OMe$-1 : 3 : 4 : 5; with hamamelase in H_2O at 37° it yields gallic acid, the 3-Me ether thereof, and glucose; with aq. $NaHCO_3$ in air it gives a mixture, whence Ac_2O yields *ellagic acid Me₂ ether diacetate* (**II**; R = R′ = Me), m.p. 287—291°, *Me₁ ether triacetate* (**II**; R = Ac, R′ = Me), m.p. 301—302°, and *tetra-acetate* (**II**; R = R′ = Ac), m.p. 344—347°.



(II.)

R. S. C.

Two types of molecules in starch. B. Brimhall and R. M. Hixon (*Wallerstein Lab. Comm.*, 1943, **6**, 95—100).—Evidence supporting the two-component theory of starch structure is presented. Methods for separating amylose (straight chain) and amylopectin (branched chain) are outlined, and the properties of these components discussed, variations between starches of different origin being noted. I. A. P.

Starch. X. End-group determination of starch components. K. Hess and B. Krajnc (*Ber.*, 1940, **73**, [*B*], 976—979).—Erythro- and amylo-amylose (Samec *et al.*, A., 1921, i, 226) give, in end-group determinations, 4·94—5·01 and 0·46—0·50%, respectively, of tetramethylglucose, indicating 23·3—23·4 and 229—247 units per mol., respectively, whereas η in $CHCl_3$ indicates 113—129 and 213—283 units, respectively. R. S. C.

Characterisation of components of starch. J. F. Foster (*Iowa State Coll. J. Sci.*, 1943, **18**, 36—38).—Mol. wts. of various amyloses have been determined from viscosity measurements and are related to the potentials at which I is taken up. Osmotic behaviour of amylose and amylopectin has also been investigated. F. R. G.

Starch–iodine complex. R. R. Baldwin (*Iowa State Coll. J. Sci.*, 1943, **18**, 10—12).—Absorption spectra of the starch–I complex under varying conditions indicate that the I atoms have definite positions in the starch helix. From these results deductions concerning the structure of starch can be made. F. R. G.

Starch. XXV. Glycogen of native muscle. K. H. Meyer and R. Jeanloz (*Helv. Chim. Acta*, 1943, **26**, 1784—1798).—Only a part of the glycogen (**I**) of mussel muscle can be extracted with hot H_2O. The remainder is found with the coagulated proteins. This fraction can be solubilised by $CCl_3{\cdot}CH(OH)_2$ or 40% CaCl₂. These reagents do not hydrolyse the proteins or rupture chemical linkings between carbohydrate and protein but the glycogen remains insol. (**I**) therefore consists of parts sol. and insol. in H_2O. Sol. (**I**) after pptn. by MeOH contains 85% of pure (**I**) and proteins, the greater part of the latter being removable by pptn. with picric acid. Electrodialysis of (**I**) gives a fraction (*A*) sol. and limpid, an opaque fraction (*B*), and swollen particles (*C*). *A* and *B* can be freed from proteins by agitation with $CHCl_3$ but this method is not applicable to *C*, which is dissolved in 40% CaCl₂ and pptd. by I as a brown compound from which the carbohydrate is readily regenerated. There remains some (**I**) which can be solubilised with a proportion of proteins by heating with 33% $CCl_3{\cdot}CH(OH)_2$ and purified through its compound with I (fraction *D*). Even after complete purification *C* and *D* remain insol. in H_2O. (**I**), prepared by treatment with KOH at 100°, is also composed of sol. and insol. portions. P is absent from all fractions and the N content can be diminished to 0·07% by methods which do not attack chemical linkings. After dissolution in $CCl_3{\cdot}CH(OH)_2$ and pptn. by EtOH, the fractions are acetylated by Ac_2O and C_5H_5N, the difficulty increasing with the insolubility of the fraction; measurements of $\eta_{sp.}$ of these acetates in $CH_2Ph{\cdot}OH$ indicate a mol. sp. wt. $>6 \times 10^6$. Comparison of the viscosity curve of the acetates of amylopectin, amylose, and (**I**) indicates that the mol. of (**I**) is very highly branched and compact in character. The limit of degradation of *A* by β-amylase is 43—43·5% whereas the figures for *B* and *C* are 33—34% and 30—32% respectively. HCl converts (**I**) into fragments which retain their highly polymerised character. It appears therefore that the voluminous enzyme fails to penetrate the mol. of (**I**) and that certain ramifications are consequently protected. H. W.

Yeast-mannan. R. Garzuly-Janke (*J. pr. Chem.*, 1940, [ii], **156**, 45—54).—By the methods of Salkowsky (A., 1894, i, 316), Daoud *et al.* (A., 1931, 1277), and Harden *et al.* (*J.C.S.*, 1902, **81**, 1224), bakers' yeast yields mannans having $[\alpha]_D^{20}$ +90·1°, +70°, and +78°, respectively, and containing no P or N. Extraction of the yeast by H_2O at successively, room temp., 40°, and 100° (total 100—120 hr.) gives a product containing carbohydrate 85·8—87, N 0·89—0·99, P 0·08—0·09, and ash 1·00—1·18%, and having $[\alpha]_D$ +62° to +63°. Extraction with 75% H_2SO_4 at room temp. (<24 hr.) gives a product containing carbohydrate 87·6—89·5, N 1·09—1·21, P 0·12—0·18, and ash 1·91—2·00%, and having $[\alpha]_D$ +66·8° to +67·2°. Alkali extraction thus decomposes the mannan-protein or -lipin components originally present. R. S. C.

Preparation of main valency gels by net formation from cellulose molecules in solution. R. Signer and P. von Tavel (*Helv. Chim. Acta*, 1943, **26**, 1972—1978).—Methylcellulose (**I**) of mean mol. wt. 21,000 and containing 68 free OH groups per 100 glucose residues reacts with $(COCl)_2$ (**II**) in $CHCl_3$ containing p-$C_6H_4Me{\cdot}NMe_2$ (**III**) to form a main valency gel. For every such solution a definite solidification time can be determined. It is considered that a mol. of (**II**) reacts one-sidedly with a free OH of a mol. of (**I**) to give an ester chloride; the second COCl group is unable for steric reasons to react with a further OH of the same mol. of (**I**) but speedily encounters a OH of a second mol. so that oxalic ester bridges are produced between 2 macromols. The bridge building extends to a third and to further mols. and ultimately proceeds through the whole solution. With a const. ratio of 0·5 mol. of (**II**) to 1 free OH of (**I**) increase in the amount of (**III**) diminishes the solidification time and increases the rate of gel formation. With a const. ratio of 1 mol. of (**III**) per OH the time of solidification is short with 0·5 mol. of (**II**), much greater in presence of 1 mol., whilst further increase in the proportion of (**II**) prevents gel formation. With 1 mol. of (**II**) per OH the time of solidification diminishes sharply with increasing concn. of (**III**). It appears that (**III**) also facilitates the reaction: $OR{\cdot}CO{\cdot}COCl + OR'{\cdot}CO{\cdot}COCl \rightarrow OR{\cdot}CO{\cdot}CO{\cdot}OR' + (COCl)_2$ [R and R′ are glucose residues of different mols. of (**I**)]. Simultaneous variation of (**II**) and (**III**) shows the influences which have been studied separately (see above) to be superimposed. The time of solidification increases as the concn. of (**I**) diminishes in the const. presence of 0·5 mol. of (**II**) and 2 mols. of (**III**) per OH. The transition sol → gel occurs the more rapidly as the distance between the thread mols. in the solution diminishes. In solutions with higher concn. of (**I**) solidification occurs simultaneously through the entire solution whereas in more dil. solution a solid surface layer is first produced which later extends to the lower portions. Net formation is also observed with succinyl, glutaryl, and sebacyl chlorides and partly acetylated celluloses may be used in dioxan. Withdrawal of solvent and reswelling of these systems occurs exactly as with isotropic, main valency gels. H. W.

Kinetics of oxidation of cellulose with periodic acid.—See A., 1944, I, 41.

End-group content of natural ramie. K. Hess and K. P. Jung (*Ber.*, 1940, **73**, [*B*], 980—983).—No tetramethylglucose is obtained from ramie by end-group determinations if degradation is avoided during its prep. R. S. C.

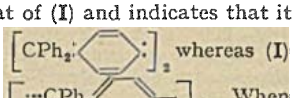
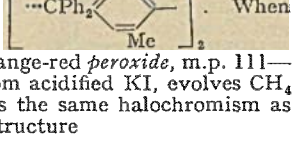
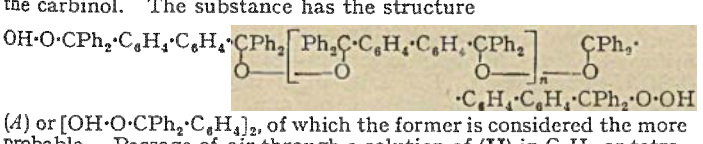
III.—HOMOCYCLIC.

Spectral characteristics and configuration of stereoisomeric carotenoids including prolycopene and pro-γ-carotene. L. Zechmeister, A. L. LeRosen, W. A. Schroeder, A. Polgár, and L. Pauling (*J. Amer. Chem. Soc.*, 1943, **65**, 1940—1951).—Steric conditions preclude more than 5 ethylenic linkings becoming *cis* in the β-carotene series, 6 in the γ-carotene, or 7 in the lycopene series. The denomination "all-*cis*" refers to these max. Change of the all-*trans* to a one-*cis* compound shifts the absorption max. by 4—6 mμ. Pro-carotenoids have "available" one-*trans* linking, since melting and chromatography reveals compounds having max. at still shorter λ. The isomerides in the lycopene series are investigated in detail; not all have the "*cis*-peak" (A., 1944, II, 9). For lycopene in light petroleum the band at ~470 mμ. is due to the electron transition $0 \rightarrow 1$, corresponding to oscillation of the "unsaturation" electrons between the ends of the chain; the *cis*-peak is due to the $0 \rightarrow 2$ transition and oscillation between the centre and ends of the chain; the ~270 mμ. band is due to the $0 \rightarrow 3$ transition and oscillation between (*a*) the first and third and (*b*) second and fourth quarters of the chain. Lycopene isomerides having a vertical plane of symmetry should have an intensity at the main absorption band <~80% of that of the all-*trans*-compound; this is the case for several known isomerides. The *cis*-peak does not exist for compounds having a centre of symmetry; its intensity depends on the distance between the *cis*-linking and the straight line joining the two ends of the chain; it is thus a max. for the compound in which the central C:C is *cis* and the others *trans* (in the lycopene series, neolycopene-*A*). The intensity of the $0 \rightarrow 3$ max. ∝ approx. that of the main max. but is less for compounds which are twice bent. Further considerations allow prediction of the ease of isomerisation, *e.g.*, that the central C:C is easiest to isomerise. Equilibrium amounts of isomerides are 10^{-x}, x being the no. of *cis*-linkings, which accounts for the limited no. of isomerides isolated. R. S. C.

Physical data of alkylcyclohexanes. A. W. Schmidt and A. Grosser (*Ber.*, 1940, **73**, [*B*], 930—933).—The following -cyclo*hexanes* are obtained by hydrogenation (PtO_2 in warm AcOH) of the requisite alkylbenzenes; the process is often irregular and generally very slow, re-activation of the catalyst being frequently necessary: n-*butyl*-, b.p. 64°/12 mm.; n-*heptyl*-, b.p. 109—110°/12 mm., m.p. 41°; n-*dodecyl*-, b.p. 131—132°/0·8 mm., m.p. 12°; n-*tetradecyl*-, b.p. 155°/0·8 mm., m.p. 25°; n-*hexadecyl*-, b.p. 163—164°/1·5 mm., m.p. 32·5°. Vals. of *d*, *n*, and η are recorded. H. W.

Methylation of benzene. A. Klit (5 *Nordiske Kemikermøde*, 1939, 217—218).—MeCl and *m*-xylene ($AlCl_3$–HCl) do not give 1 : 2 : 3-$C_6H_3Me_3$ or 1 : 2 : 3 : 4-$C_6H_2Me_4$. The equilibrium mixture from *o*-xylene (I) ($AlCl_3$–HCl) does not contain (I). M. H. M. A.

Syntheses of one-, two-, and three-nuclear hydrocarbons with 22 carbon atoms. N. Turkiewicz (*Ber.*, 1940, **73**, [*B*], 861—866).—*p*-Cymene (I) and lauryl chloride are converted by $AlCl_3$ in CS_2 into *carvacryl undecyl ketone* (II), m.p. 40·5°, b.p. 168—170°/1 mm., reduced (Clemmensen) with difficulty to 2-*dodecyl*-p-*cymene*, b.p. 163—164°/1 mm. Reduction (Raney Ni–H_2 at 230—240°/148 atm.; decahydronaphthalene) of (II) affords 2-*dodecyl*-p-*menthane*, b.p. 159—160°/1 mm. Di*iso*amylacetyl chloride, (I), and $AlCl_3$ in CS_2 give *carvacryl di*isoamylmethyl *ketone*, b.p. 162°/1 mm., reduced (Raney Ni) to *α-hexahydrocarvacryl-β-di*isoamylethane [4-iso*propyl*-2-*ββ′-di*isoamylethylhexahydrotoluene], b.p. 150—152°/1 mm. (I) is converted by CH_2O and HCl in presence of anhyd. $ZnCl_2$ and $NiCl_2$ into carvacrylmethyl chloride (IV), converted by Mg and CO_2 into *αβ*-dicarvacrylethane (III), b.p. 155—156°/1 mm., and carvacrylacetic acid, m.p. 69—70°; the corresponding Et ester, b.p. 136°/2 mm., and 1-$C_{10}H_7$·MgBr afford 1-*naphthyl carvacrylmethyl ketone*, b.p. 195—198°/0·5 mm., hydrogenated at 240—260°/150 atm. in decahydronaphthalene containing Raney Ni to *α-hexahydrocarvacryl-β*-1-*decahydronaphthylethane*, b.p. 165—166°/1 mm. (III) is obtained from (IV) and Na in boiling Et_2O and is hydrogenated at 240—260°/120—160 atm. in presence of Raney Ni to *αβ-dihexahydrocarvacrylethane*, b.p. 150—154°/1 mm. 1-$C_{10}H_7$·MgBr and lauronitrile give *α-napthyl undecyl ketone*, reduced to 1-*dodecyldecahydronaphthalene*, b.p. 170—171°/1 mm. H. W.

***pp′*-Diradical of diphenyl of the type of triphenylmethyl. II.** W. Theilacker and W. Ozegowski (*Ber.*, 1940, **73**, [*B*], 898—908; cf. A., 1940, II, 270).—Comparison of the absorption curves of 4 : 4′-dihydroxydiphenylmethyldiphenyl, its 2 : 2′-Me_2 derivative, and CPh_3·OH in conc. H_2SO_4 shows them to be generally similar. Similarly the absorption curves of 2 : 2′-dimethyl-4 : 4′-diphenylenebisdiphenylmethyl (I) and CPh_3 in C_6H_6 are closely alike and indicate that the two halves of the former are not optically independent of one another. The spectroscopic behaviour of the Tschitschibabin hydrocarbon (II) differs from that of (I) and indicates that it has predominatingly the quinonoid form  whereas (I) is predominatingly the diradical,  . When exposed to air crystals of (II) give an orange-red *peroxide*, m.p. 111—112°, which immediately liberates I from acidified KI, evolves CH_4 from MgMeI, and in conc. H_2SO_4 gives the same halochromism as the carbinol. The substance has the structure  (*A*) or $[OH·O·CPh_2·C_6H_4]_2$, of which the former is considered the more probable. Passage of air through a solution of (II) in C_6H_6 or tetrahydronaphthalene causes a change of colour with gradual separation of a *peroxide*, m.p. 156—171° according to the mode of prep.; this slowly liberates I from acidified KI, evolves CH_4 from MgMeI, and in conc. H_2SO_4 gives the same halochromism as the carbinol. Analytical results indicate the formula *A* with $n > 10$. (I) and (II) behave similarly towards O_2. Since all the available evidence points against the existence of a true diradical in (II) it is doubtful whether the behaviour towards O_2 is a true criterion of diradical nature. H. W.

Reactions of tetrahydrophenanthrene. II. W. E. Bachmann and M. W. Cronyn (*J. Org. Chem.*, 1943, **8**, 456—465).—A mixture of γ-1- and -2-naphthylbutyric acid is treated with PCl_5 in C_6H_6 at room temp. and then at 100° followed by $SnCl_4$ in C_6H_6 at 5—10° and hydrolysis, thereby giving a mixture of 1- and 4-ketotetrahydrophenanthrene (85% yield), reduced to 1 : 2 : 3 : 4-tetrahydrophenanthrene (I) in 90% yield. AcCl is added to anhyd. $AlCl_3$ in CS_2 followed by $(CHCl_2)_2$; the mixture is warmed at 45—50° until the $AlCl_3$ has dissolved completely to a green solution, which is cooled to 15° and treated with (I) in CS_2; the product is hydrolysed to 9-*acetyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (II), b.p. 163—166°/0·1 mm., m.p. 56·5—58°. Successive additions of AcCl in $PhNO_2$ to $AlCl_3$ at 5° and (I) in $PhNO_2$ at −14° give (II) and 7-*acetyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (III), m.p. 90·5—91·5°, reduced (Zn–Hg and HCl in boiling AcOH–PhMe) to 7-*ethyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (*picrate*, m.p. 90—91°), dehydrogenated (Pd–C at 300—320°) to 7-ethylphenanthrene, m.p. 65—66° (picrate, m.p. 93·5—94·5°). 7-*Bromoacetyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, from (III) and Br in abs. Et_2O at −15° to −5°, m.p. 115·5—116·5°, is converted by condensation with $CHNa(CO_2Et)_2$ followed by hydrolysis and decarboxylation of the product into β-1 : 2 : 3 : 4-tetrahydrophenanthryl-7-propionic acid, m.p. 155·5—157°. Addition of (I) in CS_2 to a solution of $AlCl_3$ and BzCl in the same solvent leads to 9-*benzoyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, m.p. 120—121°, the *oxime*, m.p. 228—229°, of which is converted by PCl_5 in boiling C_6H_6 into 1 : 2 : 3 : 4-*tetrahydrophenanthrene*-9-*carboxylanilide* (IV), m.p. 240—241°, also obtained from the acid chloride and NH_2Ph. Similarly (I), EtCOCl, and $AlCl_3$ in CS_2–$C_2H_2Cl_4$ afford 9-*propionyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, b.p. 160—162°/0·05 mm., m.p. 43—44°, reduced (Clemmensen) to 9-*propyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, m.p. 25—25·5° (*picrate*, m.p. 106—107°), which is dehydrogenated (Pd–C at 300—320°) to 9-propylphenanthrene, m.p. 58·5—59·5° (picrate, m.p. 95·5—96°). Dropwise addition of Br in C_6H_6 to (I) in C_6H_6 containing reduced Fe leads to 9-*bromo*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, b.p. 142—145°/0·05 mm. (*picrate*, m.p. 102—103°), converted by CuCN in C_5H_5N at 215—225° into the 9-*CN*-compound, m.p. 124—125°, which is hydrolysed by protracted action of boiling KOH–MeOH to 1 : 2 : 3 : 4-*tetrahydrophenanthrene*-9-*carboxylic acid*, m.p. 215—216° (*Me* ester, m.p. 70·5—71°). (I), paraformaldehyde, AcOH, HCl, and 85% H_3PO_4 at 80—85° yield 9-*chloromethyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (V), b.p. 163—165°/0·05 mm., m.p. 60·5—61°, which in boiling aq. $COMe_2$ containing KCN passes into 1 : 2 : 3 : 4-*tetrahydrophenanthryl*-9-*acetonitrile*, m.p. 89·5—90°, hydrolysed by HCl–AcOH to the -9-*acetic acid* (VI), m.p. 153—153·5°, also obtained by hydrolysis of the -9-*acetamide*, m.p. 211·5—212·5°, obtained by the Willgerodt method from (II). Treatment of (IV) with PCl_5 in C_6H_6 and of the product with anhyd. $SnCl_2$ and dry HCl in Et_2O–$C_2H_4Cl_2$ followed by hydrolysis leads to 1 : 2 : 3 : 4-*tetrahydrophenanthrene*-9-*aldehyde*, m.p. 128·5—129°, which condenses with $CH_2(CO_2H)_2$ in C_5H_5N at 100° to β-1 : 2 : 3 : 4-*tetrahydrophenanthryl*-9-*acrylic acid*, m.p. 226·5—227·5°, reduced (Na–Hg) to the -9-*propionic acid*, m.p. 168—169° (*Me* ester, m.p. 49—50°), which is also obtained from (V) by aid of $CH_2(CO_2Et)_2$. The *oxime*, m.p. 157—158°, of (III) is transformed by PCl_5 in boiling C_6H_6 into 9-*acetamido*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, m.p. 191—192°, hydrolysed by boiling HCl–EtOH to the 9-*amine*, m.p. 76·5—77° (*hydrochloride*, m.p. 263—264°). 7-*Acetamido*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, m.p. 136—137°, and the non-cryst. 7-amine (*hydrochloride*, m.p. 238—239°) are obtained similarly from the mixture of Ac derivatives (see above). The following are obtained by similar methods: 1 : 2 : 3 : 4-*tetrahydrophenanthrene*-7-*carboxylic acid*, m.p. 184—186° (*Me* ester, m.p. 114—115°); 1 : 2 : 3 : 4-*tetrahydrophenanthryl*-7-*acetamide*, m.p. 210—211°, and -*acetic acid*, m.p. 150—151°. (VI) is converted by $SOCl_2$ in dry Et_2O containing a little C_5H_5N at room temp. into the chloride, cyclised by $AlCl_3$ in C_6H_6 to 4-*keto*-7 : 8 : 9 : 10-*tetrahydroacephenanthrene*, m.p. 158·5—160°, which is reduced (Clemmensen) to 7 : 8 : 9 : 10-tetrahydroacephenanthrene, m.p. 89—90° (picrate, m.p. 111—112°).

1 : 2 : 9 : 10-Tetramethylanthracene. R. B. Sandin, R. Kitchen, and L. F. Fieser (*J. Amer. Chem. Soc.*, 1943, **65**, 2018—2020).—1 : 2-Dimethylanthraquinone (modified prep.), m.p. 157·5—158·5°, with MgMeI–Et_2O and then HI (50%)–HBr (*d* 1·4)–MeOH gives impure, yellow, amorphous (?) 1 : 2 : 9-trimethyl-10-iodomethylanthracene (I), which with NaOMe–MeOH at 60—70° yields (?) 1 : 2 : 9-*trimethyl*-10-*methoxymethylanthracene* (II), yellow, fluorescent, m.p. 124·5—125·5° [*compound*, m.p. 142·5—143·5°, with *s*-$C_6H_3(NO_2)_3$], and (?) 9-*methoxy*-1 : 2 : 9-*trimethyl*-9 : 10-*dihydroanthracene*, non-fluorescent, colourless, m.p. 141—142° [with a drop of HCl in MeOH gives (II)]. $SnCl_2$–conc. HCl–dioxan at the b.p. reduces (I) to yellow 1 : 2 : 9 : 10-tetramethylanthracene, m.p. 52—54° after softening, which is too unstable in air to be isolated except as *picrate*, m.p. 137—138°, or *compound*, m.p. 170·5—171·5°, with *s*-$C_6H_3(NO_2)_3$. M.p. are corr. R. S. C.

Aromatic cyclodehydration. XIV. 9 : 10-Dialkylphenanthrenes. C. K. Bradsher and S. T. Amore (*J. Amer. Chem. Soc.*, 1943, **65**, 2016—2017; cf. A., 1944, II, 10).—COR_2 with *o*-C_6H_4Ph·MgI–Et_2O and then aq. NH_4Cl gives α-2-diphenylyl*iso*propyl alcohol, m.p. 71° (lit., 75°), b.p. 145—154°/7 mm., γ-2-diphenylyl-*n*-pentan-γ-ol, b.p. 155—157°/7 mm., δ-2-*aiphenylyl*-n-*heptan*-δ-*ol* (I), m.p. 68°, b.p. 182—183°/11 mm., and ε-2-diphenylyl-*n*-nonan-ε-ol, b.p. 185—192°/8 mm., dehydrated by $KHSO_4$ at 160°. to β-2-diphenylylpropylene· (71% over-all), b.p. 125—128°/7 mm., γ-2-diphenylyl-Δ$^{\beta}$-*n*-pentene (47% over-all), b.p. 138—141°/7 mm., δ-2-diphenylyl-Δ$^{\gamma}$-*n*-heptene (71% over-all), b.p. 155—157°/8 mm., and ε-2-diphenylyl-Δ$^{\delta}$-*n*-nonene (55% over-all), b.p. 178—179°/7 mm., respectively, containing small amounts of Ph_2. Thence BzO_2H–$CHCl_3$ at 0°, followed by boiling 34% HBr, yields 9-methyl- (40%; 68% obtained from the oxide by $KHSO_4$ at 160°), m.p. 92° (picrate, m.p. 154°), 9-*methyl*-10-*ethyl*- (54%), m.p. 85° (picrate, m.p. 150°), 9-*ethyl*-10-n-*propyl*- (44%), m.p. 69° (picrate, m.p. 117°), and 9-n-*propyl*-10-n-*butyl*-*phenanthrene* (67%), m.p. 74° (picrate, m.p. 99°), respectively. With H_2SO_4 (5 drops) in boiling AcOH (15 c.c.), (I) gives 9 : 9-*di*-n-*propylfluorene*, m.p. 37—38°. R. S. C.

Acetylation of primary aromatic amines *in vivo* and *in vitro*.—See A., 1944, III, 129.

Derivatives of 1 : 2 : 4 : 5-tetrachlorobenzene. III. Amination of 2 : 3 : 5 : 6-tetrachloro-nitrobenzene and -4-nitroaniline. A. T. Peters, F. M. Rowe, and D. M. Stead (*J.C.S.*, 1943, 576—577; cf. A., 1943, II, 323).—The NO_2 and, to a smaller extent, both Cl *o* to

it in 2 : 3 : 5 : 6 : 1-$C_6HCl_4\cdot NO_2$ (**I**) are labile. With EtOH–NH_3 at 200° for 10 hr., (**I**) affords 2 : 3 : 5 : 6 : 1-$C_6HCl_4\cdot NH_2$ (61%) and 3 : 5-*dichloro*-1-*nitro*-2 : 6-*diaminobenzene* (**II**) (5·6%), m.p. 172—173° [Ac_2 derivative, m.p. 315° (decomp.), darkens 295°]; 9·7% of 1 : 3 : 5 : 6 : 2-$NO_2\cdot C_6HCl_3\cdot NH_2$ is also formed, as shown by reduction with aq. EtOH–$Na_2S_2O_4$ to the diamine, and conversion by phenanthraquinone (**III**) in AcOH into 1 : 2 : 4-*trichloro*-5 : 6 : 9′ : 10′-*phenanthraphenazine*, m.p. 262—263°. (**II**) does not condense with (**III**); reduction and then condensation of 4 : 6 : 1 : 2 : 3-$C_6HCl_2(NH_2)_3$, m.p. 121—122° (decomp.), with (**III**) gives 2 : 4-*dichloro*-1-*amino*-5 : 6 : 9′ : 10′-*phenanthraphenazine* (**IV**), m.p. 265°. 3 : 5 : 1 : 2-$C_6H_2Cl_2(NO_2)_2$ is unaltered with KNO_3–25% oleum at 130—160°. 1 : 2 : 5 : 4 : 6-$NH_2\cdot C_6HCl_2(NO_2)_2$, m.p. 170—171°, is reduced ($Na_2S_2O_4$) to 3 : 6 : 1 : 2 : 5-$C_6HCl_2(NH_2)_3$, converted by (**III**) into 1 : 4-*dichloro*-2-*amino*-5 : 6 : 9′ : 10′-*phenanthraphenazine*, m.p. ~322°, isomeric with (**IV**). Only the two Cl atoms *o* to NO_2 in 4 : 2 : 3 : 5 : 6 : 1-$NO_2\cdot C_6Cl_4\cdot NH_2$ (**V**) are labile. (**V**) with EtOH–NH_3 at 200° for 22 hr. gives 3 : 5-*dichloro*-1-*nitro*-2 : 4 : 6-*triaminobenzene* (56%), m.p. 256—257° (decomp.) [does not condense with (**III**)], and a trace of 1 : 3 : 5 : 6 : 2 : 4-$NO_2\cdot C_6Cl_3(NH_2)_2$ as shown by reduction and conversion into 1 : 2 : 4-*trichloro*-3-*amino*-5 : 6 : 9′ : 10′-*phenanthraphenazine*, m.p. >330°, darkening at 280°. A. T. P.

Action of aluminium chloride on phenol homologues. G. Baddeley (*J.C.S.*, 1943, 527—531).—PhOH (1 mol.) and $AlCl_3$ (1 mol.), warmed until evolution of HCl ceases, afford OPh·$AlCl_2$, b.p. 210°/15 mm., m.p. 183° (with H_2O gives PhOH). *p*-$C_6H_4Me\cdot O\cdot AlCl_2$ is stable at 200° for several hr., but *p*-cresol (**I**) and $AlCl_3$ (>1 mol.) at 130° for 2 hr. give some *m*-cresol (**II**). Kinetic study shows this change to be reversible and unimol. in respect of *p*-$C_6H_4Me\cdot O\cdot AlCl_2$, but bimol. in respect of the further $AlCl_3$ used. The reagent is not used up, and the unimol. velocity coeff. at a given temp. $\propto$ square root of amount of reagent present. (**I**) or (**II**) and $AlCl_3$ at 135° (34 hr.) give an equilibrium mixture containing 60·7% of (**II**) and 39·3% of (**I**). At 125°, a similar mixture results; thus the heat of isomerisation is small. *o*-Cresol (**III**) (1 mol.) and $AlCl_3$ (2 mols.) at 130° for 3 hr. give (**III**) only, but at 170° for 5 hr., intermol. change occurs and (**III**) [or (**II**) or (**I**)] gives PhOH + *m*-5-xylenol (**IV**). (**IV**) is also obtained from *m*-2-xylenol and $AlCl_3$ at 130—135°. *m*-4-Xylenol (at 115—120°) gives some *o*-3- and *p*-xylenol (**V**), but at 130—135° for 4·5 hr., (**IV**) is formed: (**V**) or *o*-4-xylenol is convertible into (**IV**), and (**V**) + (**IV**) are obtained from *o*-3-xylenol and $AlCl_3$ at 120—125°. Hemimellithenol is isomerised (quant.) to *iso*-ψ-cumenol by $AlCl_3$ at 100° for 10 hr. With $AlCl_3$, *p*- or *m*-$C_6H_4Et\cdot OH$ (at 120° or 125°, respectively) gives PhOH and 3 : 5 : 1-$C_6H_3Et_2\cdot OH$, also obtained from *o*-, *m*-, or *p*-$C_6H_4Et\cdot OH$ at 100°; C_2H_4 is probably an intermediate. 3 : 4 : 1-$C_6H_3MeEt\cdot OH$ (100°; 18 hr.) gives 3 : 5 : 1-$C_6H_3MeEt\cdot OH$. With (**I**), PhMe, and $AlCl_3$ at 135°, much decomp. and some demethylation occur, and PhOH (**I**) are isolable. Mechanisms of interconversions are suggested. Intermol. migration is associated with a high nuclear electron availability. The sequence, C_6H_6 homologues, xylenols, cresols, PhOH, is one of decreasing electron availability (nucleophilic character) in presence of excess of $AlCl_3$. A mechanism is deduced for the Scholl reaction. A. T. P.

Action of aluminium chloride on aromatic bromo-compounds. G. Baddeley and J. Plant (*J.C.S.*, 1943, 525—527).—PhBr is a brominating agent in presence of $AlCl_3$. Thus, PhBr and $AlCl_3$ at 100° give some *p*-$C_6H_4Br_2$. *p*-Cresol (**I**), PhBr, and $AlCl_3$ at 100° yield small amounts of 2 : 1 : 4-$C_6H_3BrMe\cdot OH$ (**II**), C_6H_6, higher-boiling products, and unchanged materials. PhOH similarly affords high-boiling products, but no $C_6H_4Br\cdot OH$. *o*-, *m*-, or *p*-$C_6H_4Br\cdot OH$ (**III**) (1 mol.) and $AlCl_3$ (2 mols.) at 130° afford (**III**) (~70%) and PhOH (~17%), with higher-boiling products; isomerisation of the *o*-is more facile than that of the *m*-isomeride. (**I**) (1 mol.), (**III**) (1 mol.), and $AlCl_3$ (4 mols.) at 130° yield PhOH, (**II**), higher-boiling products, and (**I**) + (**III**). At 100° for 20 hr., 3 : 1 : 4-$C_6H_3BrMe\cdot OH$ (1 mol.) and $AlCl_3$ (2 mols.) give (**I**) (3%), (**II**) (60%), and 2 : 6-*dibromo*-p-*cresol* (**IV**) (3%), m.p. 109° (obtained also from 2 : 6 : 1 : 4-$C_6H_2Br_2Me\cdot NH_2$); at 127° for 1 hr. the respective % are 8; 67, and 6. 2 : 4 : 1-$C_6H_3BrEt\cdot OH$ (p-*nitrobenzoate*, m.p. 57°) and $AlCl_3$ at 100° afford unchanged material, *p*-$C_6H_4Et\cdot OH$, and 3 : 4 : 1-$C_6H_3BrEt\cdot OH$ (**V**) (p-*nitrobenzoate*, m.p. 108°). 4 : 2 : 1-$OMe\cdot C_6H_3Br\cdot COMe$ (*semicarbazone*, m.p. 198°) is reduced (Clemmensen) to 3 : 4 : 1-$C_6H_3BrEt\cdot OMe$, b.p. 123—124°/5 mm., converted by boiling HBr (*d* 1·5)–AcOH into (**V**). With $AlCl_3$ at 130° for 1 hr., 3 : 5 : 1 : 4-$C_6H_3Br_2Me\cdot OH$ gives (**IV**); at 100° for 24 hr., some 2 : 5-*dibromo*-p-*cresol* (**VI**), m.p. 61° [probably intermediate in forming (**IV**)], is obtained also. 3 : 1 : 4-$C_6H_3BrMe\cdot OH$ and Br–AcOH give (**VI**) and 2 : 3 : 5 : 1 : 4-$C_6HBr_3Me\cdot OH$; with Cl_2–CCl_4 at room temp., (**VI**) yields 3-*chloro*-2 : 5-*dibromo*-p-*cresol*, m.p. 95°, converted by Cl_2–CCl_4 + Fe at 70—80° into 3 : 6 : 2 : 5 : 1 : 4-$C_6Cl_2Br_2Me\cdot OH$, new m.p. (177—178°. 3 : 6 : 1 : 4-$C_6H_2Br_2Me\cdot OH$ and $AlCl_3$ at 130° give (**IV**). With 2 : 6 : 4 : 1-$C_6H_2Br_2Et\cdot OH$ (p-*nitrobenzoate*, m.p. 93°), $AlCl_3$ at 120° causes some isomerisation to 3 : 5-*dibromo*-4-*ethylphenol*, m.p. 116—117° (convertible into 2 : 3 : 5 : 6 : 4 : 1-$C_6HBr_4Et\cdot OH$, m.p. 106°). 4 : 3 : 1-$C_6H_3ClBr\cdot OH$ is obtainable from 4 : 2 : 1-$C_6H_3ClBr\cdot OH$, but *o*-$C_6H_4Cl\cdot OH$ or 3 : 5 : 1 : 4-$C_6H_2Cl_2Me\cdot OH$ is not isomerised by $AlCl_3$. Br migrates to the nuclear positions of greatest electron density, as indicated by nuclear alkylation. A. T. P.

4-Diphenylyl butyrate. S. E. Hazlet and L. C. Hensley (*J. Amer. Chem. Soc.*, 1943, **65**, 2041).—This *ester*, m.p. 59—60·3°, is prepared (81%) from *p*-$C_6H_4Ph\cdot OH$ and PrCOCl in C_5H_5N-dioxan. R. S. C.

Triterpenes. LXXXI. Synthesis of 3-hydroxy-1 : 2 : 5-trimethylnaphthalene and of 1 : 2 : 6-trimethylphenanthrene. L. Ruzicka, E. Rey, and W. J. Smith (*Helv. Chim. Acta*, 1943, **26**, 2057—2065).—Successive addition of 1 : 2 : 3-$C_6H_3Me_2\cdot OMe$ and $(CH_2\cdot CO)_2O$ to $AlCl_3$ in $PhNO_2$ at 0° gives γ-*keto*-γ-4-*methoxy*-2 : 3-*dimethylphenyl*-n-*butyric acid*, m.p. 178°, reduced (Zn–Hg in AcOH–conc. HCl) to γ-4-*methoxy*-2 : 3-*dimethylphenyl*-n-*butyric acid*, m.p. 122—123°; the acid chloride ($SOCl_2$) could not be cyclised satisfactorily by $AlCl_3$ in CS_2 but the acid and P_2O_5 in boiling C_6H_6 give 1-*keto*-7-*methoxy*-5 : 6-*dimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (**I**), m.p. 78° [*semicarbazone*, m.p. 243° (decomp.)]; attempted cyclisation with 80% H_2SO_4 at 120—130° results also in hydrolysis to the 7-*OH*-compound, m.p. 203° [*semicarbazone*, m.p. 243° (decomp.)]. (**I**) is converted by an excess of MgMeI in Et_2O followed by treatment of the product with a little I at 140° and dehydrogenation by Se at 330° into 3-*methoxy*-1 : 2 : 5-*trimethylnaphthalene*, m.p. 106—107° [unstable picrate, m.p. 150—151·5° (decomp.)]; this is demethylated by HBr in AcOH to the 3-*OH*-compound, m.p. 140—141° (slight decomp.) (unstable picrate). 4-Methyl*cyclo*hexanone is converted by Mg β-2 : 3-dimethylphenylethyl bromide into β-1-hydroxy-4-methyl*cyclo*hexyl-α-2 : 3-dimethylphenylethane, b.p. 130—160°/0·1 mm., dehydrated and cyclised by P_2O_5 to 1 : 2 : 6-trimethyl-5 : 6 : 7 : 8 : 9 : 10 : 13 : 14-octahydrophenanthrene, b.p. 117—120°/0·06 mm., which is dehydrogenated by Se at 320° to 1 : 2 : 6-*trimethylphenanthrene*, m.p. 128·5—129° (*picrate*, m.p. 167—168°). This is oxidised by CrO_3 in AcOH at room temp. to 1 : 2 : 6-*trimethylphenanthraquinone*, m.p. 207—208° (*quinoxaline* derivative, m.p. 181—182°). M.p. are corr. H. W.

Antibacterial action of stilbene derivatives. G. Brownlee, F. C. Copp, W. M. Duffin, and I. M. Tonkin (*Biochem. J.*, 1943, **37**, 572—577; cf. A., 1944, III, 144).—*p*-Methoxydeoxybenzoin is reduced (Zn–Hg, aq. HCl) to *p*-methoxydibenzyl, which with MgMeI at 180—200° gives *p*-hydroxydibenzyl (cf. Späth, A., 1914, i, 1). α-Ethyldeoxybenzoin with Et_2O–MgEtBr affords α-*hydroxy*-αβ-*diethyldibenzyl* [αβ-*diphenyl*-α-*ethyl*-n-*butyl alcohol*], b.p. 182—186°/14 mm., dehydrated (PCl_3) to $(CPhEt{:})_2$, b.p. 170°/15 mm. (cf. Carlisle and Crowfoot, A., 1941, I, 103), reduced (H_2–PtO_2–$COMe_2$) to $(CHPhEt)_2$, m.p. 83—84° (lit. 88°, 92—93°). COPhEt and Al–Hg in wet Et_2O afford $(CPhEt\cdot OH)_2$, m.p. 135—136° (lit. 138—139°). *p*-Methoxy-αβ-diethylstilbene, m.p. 79—80° (from distillation of δ-phenyl-γ-anisylhexan-γ-ol), is reduced (H_2, Pd–C, $COMe_2$) to p-*methoxy*-αβ-*diethyldibenzyl*, m.p. 89—90°; demethylation (MgMeI) affords *p*-hydroxy-αβ-diethylstilbene, m.p. 125—127°, and p-*hydroxy*-αβ-*diethyldibenzyl*, m.p. 139—140° [*benzoate*, m.p. 110°; *O*-SO_2N-derivative (C_5H_5N salt, m.p. 195—196°)], respectively. 4-*hydroxy*-4′-*methoxy*-αβ-*diethylstilbene*, m.p. 101—102°, is obtained as a by-product during demethylation of the Me_2 ether. *p*-Nitrodeoxybenzoin and EtI in boiling EtOH–NaOEt yield p-*nitro*-α-*ethyldeoxybenzoin*, m.p. 78—80°, reduced (Fe–$FeCl_3$–H_2O–xylene) to the NH_2-compound, m.p. 128—129°, which with MgEtBr gives p-*amino*-β-*hydroxy*-αβ-*diethyldibenzyl*, m.p. 91—92°, converted by AcOH–HCl into p-*amino*-αβ-*diethylstilbene hydrochloride*, m.p. 254—255°; the corresponding *base*, m.p. 96—97°, with *p*-$NHAc\cdot C_6H_4\cdot SO_2Cl$ in C_5H_5N yields the *Ac* derivative, m.p. 207—208°, of p-*sulphanilamido*-αβ-*diethylstilbene*, m.p. 180—182°. 4′-Nitro-4-hydroxystilbene is reduced (EtOH–aq. NH_3–$FeSO_4$ at b.p.) to 4′-*amino*-4-*hydroxystilbene*, m.p. 270—271° (decomp.). *p*-$CN\cdot C_6H_4\cdot CH_2\cdot CO_2H$ with *p*-$OH\cdot C_6H_4\cdot CHO$ and piperidine at 140° gives 4-*hydroxy*-4′-*cyanostilbene*, m.p. 221—223°, converted (method: Ashley *et al.*, A., 1942, II, 172) into 4-*hydroxy*-4′-*amidinostilbene hydrochloride*, m.p. 316—317° (decomp.). F. O. H.

Formation of phenols by the action of hydrogen peroxide on nonphenolic, aromatic aldehydes. E. Spath, M. Pailer, and G. Gergely (*Ber.*, 1940, **73**, [*B*], 935—938).—Shaking 100-vol. aq. H_2O_2 with Et_2O and drying gives 2% H_2O_2–Et_2O, whence evaporation gives ~4—6% H_2O_2–Et_2O. This reagent (1·1 mol. of H_2O_2) with ArCHO at 20° (~15 hr.), sometimes with $CHCl_3$ or more Et_2O, gives (i) 2 : 4 : 1-$(OMe)_2C_6H_3\cdot OH$ (26·1%) (no acid is formed), (ii) 2 : 4 : 5 : 1-$(OMe)_3C_6H_2\cdot OH$ (17·6%) and -$(OMe)_3C_6H_2\cdot CO_2H$ (trace), (iii) 3 : 4 : 6 : 1-$(OMe)_2C_6H_2Et\cdot OH$ (13·7) and -$(OMe)_2C_6H_2Et\cdot CO_2H$ (4·2%), (iv) *p*-$OMe\cdot C_6H_4\cdot OH$ (7·1) and *p*-$OMe\cdot C_6H_4\cdot CO_2H$ (6·5%), (v) *o*-$OMe\cdot C_6H_4\cdot OH$ (6·6) and *o*-$OMe\cdot C_6H_4\cdot CO_2H$ (4·7%), (vi 3 : 4 : 1-$(OMe)_2C_6H_3\cdot OH$ (1·4) and -$(OMe)_2C_6H_3\cdot CO_2H$ (4·0%), and (vii) PhOH (0·7) and BzOH (8·6%). ArCHO not thus accounted for is mainly recovered unchanged. $OH\cdot CHAr\cdot O_2H$ may be intermediates. R. S. C.

Synthesis and structure of ψ-cumoqumol monoalkyl ethers. W. John and F. H. Rathmann (*Ber.*, 1940, **73**, [*B*], 995—1001).—ψ-Cumoquinol, 2 : 3 : 5 : 1 : 4-$C_6HMe_3(OH)_2$ (**I**), with MeOH–H_2SO_4 at room temp. gives the 1-*Me ether* (**II**), m.p. 101°; Me_2SO_4 gives

mainly the Me_2 ether with a little (**II**). 1 : 2 : 5 : 3-$C_6H_2Me_3$·OMe (prep. by Me_2SO_4) with 1 : 2 HNO_3 (*d* 1·52)–AcOH at ~30° gives the 6-NO_2-, m.p. 107—108°, reduced by Sn–conc. HCl–EtOH to the 6-NH_2-derivative (**III**), m.p. 75° (*hydrochloride*, decomp. >230°; impure stannichloride, m.p. 213—215°), whence diazotisation in 0·5N-HCl and heating at 75° gives (**II**). In boiling 90% HCO_2H 3 : 1 : 2 : 5 : 6-OH·C_6HMe_3·NH_2 gives 6-*formamido*iso-ψ-*cumenol*, m.p. 216—219°, which with Me_2SO_4 gives the N-*CHO* derivative, m.p. 178—179°, of (**III**), hydrolysed to (**III**) by conc. HCl. 1 : 2 : 5 : 3-$C_6H_2Me_3$·OH and 1 : 4 HNO_3 (*d* 1·52)–AcOH at room temp. to 45° give the $(NO_2)_2$-derivative, m.p. 134·5° (K and Na salts; *Me*, m.p. 96°, and *Et ether*, m.p. 92°, prepared from the *Ag* salt), but no $(NO_2)_1$-derivative could be obtained. With ROH–H_2SO_4, (**I**) gives the 1-*Et*, m.p. 87—88° [*acetate* (**IV**), m.p. 57—58°; *propionate*, m.p. 40—41°], -*Pr*, m.p. 78°, -*Bu*$^{\alpha}$ (80%; 20—30% obtained by BuBr–NaOEt–EtOH), m.p. 68°, and -iso*amyl ether*, m.p. 51°. (**IV**) is physiologically inactive. R. S. C.

Constituents of red sandalwood. II. Constitution of pterostilbene. E. Spath and J. Schlager (*Ber.*, 1940, **73** [*B*], 881—884; cf. A., 1940, II, 286).—The freely sol. portion of the Et_2O extract of red sandalwood is treated with hot CCl_4. The residue after removal of the solvent is dissolved in Et_2O and fractionally extracted with aq. KOH; the alkaline extracts are acidified and extracted with Et_2O, and the residue from this extract is cryst. from Et_2O–light petroleum, thus giving *pterostilbene* [4-*hydroxy*-3′ : 5′-*dimethoxystilbene*] (**I**), m.p. 85—86°, *a* 0. (**I**) contains 2 OMe. It is converted by CH_2N_2 into *pterostilbene Me ether* (**II**), m.p. 56—57°. (**I**) quantitatively absorbs 1 H_2 in AcOH containing Pd sponge. Oxidation of (**I**) and (**II**) gives 3 : 5 : 1-$(OMe)_2C_6H_3$·CO_2H (**III**) and *p*-OMe·C_6H_4·CO_2H with (**III**) respectively. H. W.

Hexahydroxybenzene and its derivatives. I. E. Neifert and E. Bartow (*J. Amer. Chem. Soc.*, 1943, **65**, 1770—1772).—1 : 2 : 3 : 5 : 6 : 4-O:$C_6(OH)_4$:O is obtained (80%) from the Na_2 salt (prep. from *i*-inositol by conc. HNO_3 and then $NaHCO_3$) by 1 : 10 45% HI–37% HCl, and with 45% HI (3 pts.) in boiling EtOH (10 pts.) gives ~70% of $C_6(OH)_6$. This yields a hexa-acetate, m.p. 203°, -*propionate*, m.p. 133°, -n-, m.p. 135°, and -iso-*butyrate*, m.p. 164·5°, -n-, m.p. 103°, and -iso-*valerate*, m.p. 155°, -n-*hexoate*, m.p. 97°, -n-*octoate*, m.p. 86°, -n-*decoate*, m.p. 85°, -*chloroacetate*, m.p. 212°, -*trichloroacetate*, m.p. 245°, (decomp.), and -benzoate, m.p. 254°. In 50% EtOH it gives *compounds*, $C_6(OH)_6$,$2NH_2Ar$, in which Ar = Ph, *o*-, *m*-, and *p*-tolyl, *m*- and *p*- (not *o*-)C_6H_4Cl, and a *compound*, $C_6(OH)_6$,NH_2·C_6H_4Me-*o*. R. S. C.

Preparation of fluoreneazo-dyes. W. Bielenberg, H. Goldhahn, and H. Pluskal (*Ber.*, 1940, **73**, [*B*], 878—881).—The following 2-*fluoreneazo*-dyes are obtained by mixing equiv. amounts of 2-fluorenediazonium chloride (**I**) and the requisite phenol with at least 3 equivs. of KOAc in EtOH and purifying the product by repeated dissolution in EtOH and pptn. by H_2O: -*phenol*, m.p. 187·5—191°; -m-, -o-, and -p-*cresol*, m.p. 200°, 173—174°, and 143—144°, respectively; -*thymol*, m.p. 164—164·5°; -*guaiacol*, m.p. 145—146°; -*resorcinol*, m.p. 204—204·5°, decomp. at a slightly higher temp.; -*orcinol*, m.p. 220—221°; -m-4-*xylenol*, m.p. 179—180°; -*phloroglucinol*, softens at 215° and decomposes at a higher temp.; -*pyrogallol*, no distinct m.p. (**I**) and *o*-$C_6H_4(OH)_2$ give a product, m.p. 172—173°; an almost colourless, unidentified compound, m.p. 112—113°, is formed from *o*-$C_6H_4(OAc)_2$ but normal coupling occurs with *o*-OH·C_6H_4·OBz to the benzoate, m.p. 223°, of 2-*fluoreneazopyrocatechol*, m.p. 175°. H. W.

Lignin and related compounds. LXXII. Ultra-violet absorption spectra of compounds related to lignin.—See A., 1944, I, 28.

Constitution of the internal diazo-oxides (diazo-phenols and -naphthols). H. H. Hodgson and E. Marsden (*J. Soc. Dyers and Col.*, 1943, **59**, 271—275).—Previous views on the constitution of the diazo-oxides are reviewed and it is concluded that they are not internal cyclic oxides but resonance hybrids whereas the more stable *o*-diazosulphides are true cyclic compounds. Supporting evidence is adduced from (*a*) coupling, especially in acid solution, (*b*) replacement by H, (*c*) a new bromination reaction in which 6-nitronaphthalene-2 : 1-diazo-oxide affords 6 : 2 : 4 : 1-NO_2·$C_{10}H_4Br_2$·OH via the diazoperbromide, and (*d*) the action of $ZnCl_2$ or $SbCl_3$ in EtOH on diazo-oxides made from *p*-NH_2·C_6H_4·OH, *p*-NH_2·C_6H_4·SO_3H, 1 : 8 : 3 : 6-NH_2·$C_{10}H_4(OH)(SO_3H)_2$, 1 : 8 : 4-NH_2·$C_{10}H_5(OH)$·SO_3H, 2 : 1- and 1 : 2-NO_2·$C_{10}H_6$·NH_2, 2 : 4 : 1- and 1 : 6 : 2-$(NO_2)_2C_{10}H_5$·NH_2; these do not give isolable double salts (considered to be formed) and are recovered unchanged on dilution with H_2O when SO_3H is not present and giving *Zn* salts of the sulphonic acids. The diazo-oxides do not afford periodides with KI but either replace N_2 by I or give K salts of the diazo-oxide sulphonic acids. K. H. S.

Catalytic debenzylation. Effect of substitution on the strength of the *O*- and *N*-benzyl linkings. R. Baltzly and J. S. Buck (*J. Amer. Chem. Soc.*, 1943, **65**, 1984—1992).—The effects of substitution on catalytic debenzylation (Pd–C–H_2; usually in EtOH or MeOH) are investigated by observing the rates of hydrogenolysis of CHArR·OH and COArR etc. and by isolating the products of competitive hydrogenolysis of the hydrochlorides (bases not reduced) of CH_2Ar·NH·CH_2Ar or CH_2Ar·NMe·CH_2Ar. R = alkyl or OH-alkyl reduces the rate of reaction; R = CO·NH_2 or CO_2H prevents it; the exact effect of R = CN or Ph is uncertain, but hydrogenolysis proceeds normally. Benzoin and α-diketones are readily reduced. Reductions of C:C and CH_2·OH in CHPh:CH·CH_2·OH proceed at approx. the same rate. Substitution in Ar of OMe, OH, NH_2, Cl, NR_3Cl, or Me increases the stability. *a*- or *β*-$C_{10}H_7$·CH_2 is removed in preference to CH_2Ph, this being the only case in which the ease of removal of CH_2Ph is exceeded; its preparative usefulness is limited to special cases. Ephedrine is not reduced. Hydrogenation of COPhEt in presence of an inefficient catalyst and NH_4Cl gives 85% of CHPhEt·OH [Hartung]. *Hydrochlorides* (m.p. in parentheses) of the following are described: *o*- (123—123·5°) and *m*-methoxybenzyl- (128·5—129°), 4-diphenylylmethyl- [265° (decomp.)], and α-naphthylmethyl-methylamine (189·5—190°); 4-methoxy-3′ : 4′-methylenedioxy- (246—247°) and -4′-hydroxy-dibenzylamine (179—179·5°); 2 : 4′- (160—161°) and 3 : 4′-dimethoxy- (159—160·5°), 4-methyl- (161—162°), and 4-chloro-dibenzylmethylamine (145·5—146·5°); benzyl-α- (225°) and -*β*-naphthylmethylmethylamine (194—195°); α-naphthylmethyl-*β*-naphthylmethyl- (230·5—231°) and α-naphthylmethyl-4-diphenylylmethyl-methylamine (211·5—212°). *p*-Aminobenzylmethylamine (*dihydrochloride*, m.p. 201·5—202°), p-*aminomethylphenyltrimethylammonium chloride hydrochloride*, m.p. 223—223·5°, p-*dimethylaminodibenzylamine methochloride hydrochloride*, m.p. 164° (decomp.), p′-*benzyloxybenzylidene*-p-*methoxybenzylamine*, m.p. 82°, p-N-*acet*-N-*benzylamidomethylphenyltrimethylammonium chloride* (**I**), m.p. 130—130·5°, and 4-aminodibenzylmethylamine (*dihydrochloride*, m.p. 182·5—183°), are also described. (**I**) is prepared by the reactions: *p*-NMe_2·C_6H_4·CHO + CH_2Ph·NH_2 → *p*-NMe_2·C_6H_4·CH:N·CH_2Ph → *p*-NMe_2 C_6H_4·CH_2·NR·CH_2Ph (*A*; R = H) → (*A*; R = Ac) → *p*-NMe_3I· → (**I**). R. S. C.

Action of potassium on benzpinacol in boiling ether under nitrogen. L. Anschutz and (Miss) A. Ungar (*J. pr. Chem.*, 1940, [ii], **156**, 38—44).—When K is added to $(CPh_2$·$OH)_2$ (**I**) in boiling Et_2O–N_2, change in the b.p. indicates halving of the mol. wt. within 1—2 min., followed in ⩽10 min. by appearance of a blue colour due to CPh_2·OK. The first change is due to KOH present in the K decomp. (**I**) into $COPh_2$ and $CHPh_2$·OH, which later react with K to give (i) CPh_2·OK and (ii) $CHPh_2$·OK + H. Analysis (method: C., 1944, Part I) shows presence of ~80% of $CHPh_2$·OK and ~20% of CPh_2·OK, this being caused by reduction of $COPh_2$ to $CHPh_2$·OH by the liberated H. (**I**) and K react more slowly in Et_2O at room temp., in this case evolution of H_2 being visible. KOH may play a part in all formations of ketyls from pinacols. R. S. C.

Synthetic mydriatics. III. F. F. Blicke and H. M. Kaplan (*J. Amer. Chem. Soc.*, 1943, **65**, 1967—1970; cf. A., 1942, II, 237).—The following esters are prepared by heating the appropriate aminoalkyl chloride and acid in Pr$^{\beta}$OH. Mydriatic activity in 2% aq. solution is indicated by 1 poor, 2 moderate, 3 good, or 4 excellent, and anæsthetic activity by *S* slight, *G* good, or *E* excellent; absence of an entry for the salts indicates inactivity. *β*-Dipropyl- (*hydrochloride*, m.p. 116—118°) and *β*-dibutyl-aminoethyl (*hydrochloride*, m.p. 104—106°), *β*-piperidinoethyl (*hydrobromide*, m.p. 140—141°), *γ*-dibutylamino- (*hydrochloride*, m.p. 92—93°) and *γ*-piperidino-*n*-propyl (*hydrochloride*, m.p. 136—137°), *γ*-dimethylamino- [*hydrochloride*, m.p. 117—118°; *methobromide* (*S*), m.p. 145—146°], *γ*-diethylamino- (*G*), m.p. 66—67°, and *γ-piperidino-ββ-dimethyl-n-propyl* (*G*), m.p. 96—97°, *mandelate*; *β*-dimethyl- [*hydrochloride* (4, *E*), m.p. 183—185°] and *β*-dipropyl-aminoethyl [*hydrochloride* (*G*), m.p. 152—153°], *β*-diethyl- [*hydrochloride* (3, *G*), m.p. 163—164°] and *β*-dibutyl-amino-*n*-propyl [*hydrochloride* (*G*), m.p. 167—168°], *γ*-diethyl- [*hydrochloride* (4, *E*), m.p. 145—146°], *γ*-dipropyl- [*hydrochloride* (*G*), m.p. 158—159°], and *γ*-dibutyl-amino-*n*-propyl [*hydrochloride* (*G*), m.p. 114—115°; *methobromide* (*G*), m.p. 166—167°], *γ*-dimethyl- [*hydrochloride* (4, *E*), m.p. 169—170°; *methobromide* (4, *E*), m.p. 150—151°] and *γ*-diethyl-amino-*ββ*-dimethyl-*n*-propyl [hydrochloride (4, *E*), m.p. 139—140° (lit. 141—142°)] benzilate; *β*-diethylamino- (*hydrochloride*, m.p. 108—109°), *β*-dibutylamino- [*hydrochloride* (*E*), m.p. 120—121°], and *β*-piperidinoethyl [*hydrochloride* (*E*), m.p. 161—162°; *methobromide*, m.p. 149—150°], *γ*-dibutylamino- [*hydrochloride* (*G*), m.p. 93—94°] and *γ*-piperidino-*n*-propyl [*hydrochloride* (*S*), m.p. 130—131°], *γ*-dimethyl- [*hydrochloride* (3), m.p. 128—129°] and *γ*-diethyl-amino-*ββ*-dimethyl-*n*-propyl (*phosphate*, m.p. 150—151°) atrolactate; *β*-diethyl- [*methobromide* (2), hygroscopic, m.p. 99—101°] and *β*-dibutyl-aminoethyl (*methobromide*, m.p. 131—132°), *γ*-dibutylamino- (*methobromide*, m.p. 127—128°) and *γ*-piperidino-*n*-propyl [hydrochloride (2, *S*), m.p. 127—128° (lit. an oil)], *γ*-dimethyl- [*phosphate* (2), m.p. 143—144°] and *γ*-diethyl-amino-*ββ*-dimethyl-*n*-propyl [phosphate (= Syntropan) (2—3), m.p. 139—141° (lit. 138—140°)] tropate; *β*-diethylamino- (methobromide, an oil) and *β*-piperidino-ethyl (*hydrochloride*, m.p. 128—129°), *γ*-piperidino-*n*-propyl (*methobromide*, m.p. 116—118°), *γ*-dimethyl- (*methobromide*, m.p. 164—166°) and *γ*-diethyl-amino-*ββ*-dimethyl-*n*-propyl (*hydrochloride*, m.p. 99—100°) α-hydroxy-*β*-phenylpropionate; *β*-dibutyl-

amino- (*methobromide*, m.p. 129—131°) and β-piperidino-ethyl (*hydrochloride*, m.p. 102—103°; *methobromide*, m.p. 113—115°), γ-dibutylamino- (*methobromide*, m.p. 87—89°) and γ-piperidino-*n*-propyl (*hydrochloride*, m.p. 143—144°), γ-dimethyl- (*methobromide*, m.p. 117—119°) and γ-diethyl-amino-ββ-dimethyl-*n*-propyl (*hydrochloride*, m.p. 89—90°) β-hydroxy-β-phenylpropionate; β-diethylamino- [*hydrochloride* (2, *G*), m.p. 144—146°], β-dipropylamino- [*hydrochloride* (*E*), m.p. 115—116°], and β-piperidino-ethyl [*hydrochloride* (*G*), m.p. 169—171°], γ-diethylamino- [*hydrochloride* (*G*), m.p. 143—145°] and γ-piperidino-*n*-propyl [*hydrochloride* (*E*), m.p. 127—128°], and γ-dimethylamino-ββ-dimethyl-*n*-propyl [*hydrochloride* (*E*), m.p. 136—138°] β-hydroxy-ββ-diphenylpropionate. Generalities noted include the frequent but not universal concurrence of mydriatic and anæsthetic activity, irregularities among homologues, the general activity of benzilates, and the lack of or slight anæsthetic activity of tropates. $CH_2Ph{\cdot}CH(OEt)_2$, b.p. 114—120°/15 mm., is obtained (70%) from $CH_2Ph{\cdot}MgCl$ and $CH(OEt)_3$ in Et_2O and with, successively, 10% H_2SO_4, $NaHSO_3$, KCN, and 18% HCl gives $CH_2Ph{\cdot}CH(OH){\cdot}CO_2H$. β-Piperidinoethyl chloride, b.p. 69°/12 mm. [hydrochloride, m.p. 229—230° (lit., 208°, 231°)], $NBu_2{\cdot}CHMe{\cdot}CH_2Cl$, b.p. 116—120°/29 mm., $NPr_2{\cdot}[CH_2]_3{\cdot}Cl$, b.p. 99—102°, $NBu_2{\cdot}[CH_2]_3{\cdot}Cl$ (*aurichloride*, m.p. 143—146°), and $NMe_2{\cdot}CH_2{\cdot}CMe_2{\cdot}CH_2Cl$, b.p. 44—49°/14 mm., are also described. R. S. C.

Rearrangement of allyl groups in three-carbon systems. III. Nitriles and an acid. D. E. White and A. C. Cope (*J. Amer. Chem. Soc.*, 1943, **65**, 1999—2004; cf. A., 1941, II, 279).—$C{\equiv}C{\cdot}CRR'{\cdot}CH_2{\cdot}CH{:}CH_2$ (R and R' = CN or CO_2Et) rearranges at 135—200°, with inversion, to $CH_2{:}CH{\cdot}CH_2{\cdot}CH{:}C{\cdot}CRR'$. *cyclo*Hexylidenephenylacetonitrile (**I**) (modified prep.), b.p. 173—174°/10 mm., with $NaNH_2$ in liquid NH_3 gives the Na derivative, which with $CH_2{:}CH{\cdot}CH_2Br$ (**II**) in boiling Et_2O gives α-Δ¹-cyclo*hexenyl*-α-*phenyl*-Δ^γ^-*pentenonitrile* (**III**) (77%), b.p. 106—109°/0·001 mm., hydrogenation of which proceeds in two stages, giving, best with Raney Ni in EtOAc at ~200°/~130 atm., *acet*-β-Δ¹-cyclo*hexenyl*-β-*phenyl*-n-*amylamide* (**IV**) (45%), m.p. 141·5—143°. With Pr^nI instead of (**II**) in C_6H_6, (**I**) gives α-Δ¹-cyclo*hexenyl*-α-*phenyl*-n-*valeronitrile*, b.p. 147—148°/1·5 mm., hydrogenated as above to (**IV**) (53%), m.p. 140·5—142° (proof of structure). $CH_2Ph{\cdot}CN$ with $NaNH_2$–NH_3 and then *cyclo*hexyl bromide in C_6H_6 gives *cyclo*hexylphenylacetonitrile (72%), m.p. 55—55·5° (lit., 56°, 60°), b.p. 165—167°/9 mm., which by propylation as above gives α-*cyclo*hexyl-α-phenyl-*n*-valeronitrile (70%), b.p. 155—158°/3·5 mm., and thence by hydrogenation as above *acet*-β-cyclo*hexyl*-β-*phenyl*-n-*amylamide* (48%), m.p. 129—130°. At 220° in N_2, (**III**) gives 2-*allyl*cyclo*hexylidenephenylacetonitrile* (**V**) (85%), b.p. 160—162°/2 mm., the structure of which is proved as follows. (**V**) absorbs 0·996 H_2 rapidly and then slowly a further quantity. Distillation of (**V**) from KOH in aq. $(OH{\cdot}[CH_2]_2)_2O$ (**VI**) gives NH_3, $CH_2Ph{\cdot}CO_2H$ (73%), and 2-allyl*cyclo*hexanone (**VII**) (43% isolated as 2 : 4-*dinitrophenylhydrazone*, m.p. 145—146°). CHPhNa·CN and (**VII**) in boiling PhMe give 28% of (**V**) (possibly a slightly different mixture of geometrical isomerides). Heating $CN{\cdot}CH_2{\cdot}CO_2H$, *cyclo*hexanone, and NH_4OAc in C_6H_6 with removal of H_2O gives *cyclo*hexylidenecyanoacetic acid, which is decarboxylated at 130—140°/50—70 mm. to Δ¹-*cyclo*hexenylacetonitrile (79%), b.p. 99°/15 mm. This is converted by $NaNH_2$–NH_3 and then (**II**)–Et_2O at, successively, −40°, room temp., and the b.p. into α-Δ¹-cyclo*hexenyl*-Δ^γ^-n-*pentenonitrile* (**VIII**) (19%), b.p. 85—87°/1·5 mm., α-Δ¹-*cyclohexenyl*-α-*allyl*-Δ^γ^-n-*pentenonitrile* (**IX**) (40%), b.p. 107—108·5°/1·5 mm., and a *substance*, $C_{22}H_{30}N_2$, m.p. 105—106°. At 185° in N_2, (**VIII**) gives 2-*allyl*cyclo*hexylideneacetonitrile*, fractions, b.p. 121—122°/10 mm. and 122—123°/10 mm., converted by KOH as above, with much hydrolysis, into small amounts of (**VII**) and AcOH. At 175° (**IX**) gives α-2-*allyl*cyclo*hexylidene*-Δ^γ^-n-*pentenonitrile* (78%), b.p. 117—119°/2 mm., cleaved as above into (**VII**) (poor yield). Alkylation of $CH_2{:}CH{\cdot}CH_2{\cdot}CN$ as above gives α-*vinyl*-α-*allyl*-Δ^γ^-n-*pentenonitrile* (**X**) (31%), b.p. 103—104°/35 mm., which at 180° in N_2 yields α-*allyl*-Δ^αε^-*heptadienonitrile* (62%), b.p. 95—96°/13 mm., whence O_3 in EtOAc and then aq. H_2O_2 at 100° yields $(CH_2{\cdot}CO_2H)_2$. Distilling H_2O from $COEt_2$–$CN{\cdot}CH_2{\cdot}CO_2H$–$NH_4OAc$–AcOH–$C_6H_6$ and heating the product at 140—145°/40—60 mm. gives β-*ethyl*-Δ^β^-n-*pentenonitrile* (72%), b.p. 104—105°/72 mm., which by alkylation gives β-*ethylidene*-α-*allyl*-n-*valeronitrile* (38%), b.p. 69—70°/2 mm. At 195° (N_2), this gives γ-*methyl*-β-*ethyl*-Δ^αε^-*heptadienonitrile* (70%), b.p. 100—101°/11 mm., whence O_3 gives $COEt{\cdot}CHMe{\cdot}CH_2{\cdot}CO_2H$, also obtained by ozonising $COEt{\cdot}CHMe{\cdot}CH_2{\cdot}CH{:}CH_2$ in EtOAc. With KOH–(**VI**)–H_2O, (**X**) gives α-*vinyl*-α-*allyl*-Δ^γ^-n-*pentenoic acid* (54%), b.p. 108—110°/2·5 mm., rearranged at 185° (N_2) into α-*allyl*-Δ^αε^-n-*heptadienoic acid* (61%), b.p. 116—118°/1·5 mm. [with O_3 gives $(CH_2{\cdot}CO_2H)_2$]. R. S. C.

Oxidation of *o*-cresol to salicylic acid by alkali fusion. D. E. Bland (*J. Proc. Austral. Chem. Inst.*, 1943, **10**, 239—242).—Under the most favourable conditions, the method of Lock *et al.* (A., 1939, II, 113) gives ~31% of *o*-$OH{\cdot}C_6H_4{\cdot}CO_2H$. Yields of 29—39% are obtained from a dry, intimate mixture of *o*-cresol and NaOH (3 parts) at 250°/3 hr. A. T. P.

Photochemical dimerisation of *trans*-cinnamic acid. H. I. Bernstein and W. C. Quimby (*J. Amer. Chem. Soc.*, 1943, **65**, 1845—1846).—Rapidly pptd. or commercial *trans*-$CHPh{:}CH{\cdot}CO_2H$ gives only β-truxinic acid on exposure to sunlight, but after slow recrystallisation it gives α-truxilic acid. W. R. A.

Synthesis of 3-methylpyrogallolaldehyde [2 : 4-dihydroxy-3-methoxybenzaldehyde]. F. Mauthner (*J. pr. Chem.*, 1940, [ii], **156**, 154—156).—The fraction, b.p. 145—155°/12 mm., of the mixture obtained from 1 : 2 : 3-$C_6H_3(OH)_3$ (100 g.) in EtOH (200 c.c.), MeI (80 g.), and KOH (29·4 g.) in EtOH (150 c.c.) after 10 hr. at the b.p., is treated with boiling AcCl and the product fractionated. Fractional crystallisation of the material, b.p. 160—180°/12 mm., from EtOH gives 1 : 2 : 3- and 2 : 1 : 3-$OMe{\cdot}C_6H_3(OAc)_2$, m.p. 51—54° (more sol.). Hydrolysis (dil. NaOH) then affords a poor yield of 2 : 1 : 3-$OMe{\cdot}C_6H_3(OH)_2$, m.p. 85—87°, converted by $Zn(CN)_2$–Et_2O–HCl into 2 : 4-*dihydroxy*-3-*methoxybenzaldehyde*, m.p. 83—84° (p-*nitrophenylhydrazone*, decomp. 250°). H. B.

Stabilisation of keto-compounds by acetalisation.—See A., 1944, II, 33.

***cis*- and *trans*-8-Methyl-1-hydrindanone.** W. E. Bachmann and S. Kushner (*J. Amer. Chem. Soc.*, 1943, **65**, 1963—1967).—Et 1-hydroxy-2-carbethoxy-2-methyl*cyclo*hexylacetate (prep. improved to give 88% yield; cf. Chuang *et al.*, A., 1935, 859), b.p. 173—177°/18 mm., with $SOCl_2$–C_5H_5N and then KOH–MeOH gives 2-carboxy-2-methyl*cyclo*hexylideneacetic (**I**), m.p. 101·8—103·5°, and 2-*carboxy*-2-*methyl*-Δ^6^-cyclo*hexenylacetic acid* (**II**), m.p. 170·5—170·8° [? a stereoisomeride of (**I**)]. H_2–PtO_2 converts (**II**) in AcOH into *cis*-2-carboxy-2-methyl*cyclo*hexylacetic acid (**III**), m.p. 161·5—163° (A., 1943, II, 372, m.p. 163—164°), but (**I**) gives also a small amount of the *trans*-acid (**IV**), m.p. 173—174°. Treating crude (**III**) with CH_2N_2 and then NaOH–H_2O–MeOH gives *cis*-2-carbomethoxy-2-methyl*cyclo*hexylacetic acid, m.p. 54·5—60° (Chuang *et al.*, *loc. cit.*), which with $SOCl_2$ and a little C_5H_5N in C_6H_6 at 40° and then CH_2N_2–C_6H_6–Et_2O gives a diazo-ketone, converted by Ag_2O–MeOH into Me *cis*-β-2-carbomethoxy-2-methyl*cyclo*hexylpropionate, a syrup. Cyclisation by NaOMe–C_6H_6 and subsequent treatment with boiling HCl–AcOH–H_2O yields *cis*-8-methyl-1-hydrindanone, m.p. 38·2—39·5°, b.p. 121—123°/45—47 mm. (*oxime*, m.p. 85·5—87°). Hydrogenation (Raney Ni; 125—150°/1800—2000 lb.; H_2O) of K H 1-methyl-Δ^2^-*cyclo*hexene-1 : 2-dicarboxylate gives *trans*-1-methyl-*cyclo*hexane-1 : 2-dicarboxylic acid, m.p. 214—214·3° (lit. 210°), which yields, as above, trans-2-*carbomethoxy*-2-*methyl*cyclo*hexane*-1-*carboxylic acid*, m.p. 90—91·5° after softening. With $(COCl)_2$ in C_6H_6 this gives the acid chloride, which with, successively, CH_2N_2, Ag_2O–MeOH, and KOH–MeOH–H_2O yields (**IV**), m.p. 175—177·8°, which is converted, as above, into trans-8-*methyl*-1-*hydrindanone*, b.p. 108—109°/20 mm. [*semicarbazone*, m.p. 234° (bath preheated to 190°); *oxime*, m.p. 113—115·5°]. R. S. C.

Relationship between anti-mitotic action and constitution in colchicine derivatives. H. Lettré and H. Fernholz (*Z. physiol. Chem.*, 1943, **278**, 175—200; see also A., 1944, III, 92).—Colchiceine (in $CHCl_3$) and the diazoalkane (in Et_2O) give the amorphous *methyl*-, melts from ~130° (probably not identical with colchicine), *ethyl*-, melts from ~110°, *n*-propyl-, melts from 98°, and *n*-butyl-colchiceine, melts from 90°. p-*Anisyl* 3 : 4 : 5-*trimethoxystyryl ketone*, m.p. 134° [from 3 : 4 : 5 : 1-$(OMe)_3C_6H_2{\cdot}CHO$ (**I**) and *p*-$OMe{\cdot}C_6H_4{\cdot}COMe$ in EtOH + MeOH–NaOMe], is reduced (H_2, Pt-black, AcOH) to the β-3 : 4 : 5-trimethoxyphenylethyl ketone, m.p. 98°, the oxime, m.p. 102°, of which is reduced (Na–Hg, EtOH–AcOH) to α-*p*-anisyl-γ-3 : 4 : 5-trimethoxyphenylpropylamine (*Ac* derivative, m.p. 88°). *Ph* 3 : 4 : 5-*trimethoxystyryl ketone*, m.p. 137°, similarly leads to α-phenyl-γ-3 : 4 : 5-trimethoxyphenylpropylamine (*Ac* derivative, m.p. 137—138°). N-*Acetyl*-α-p-*anisyl*-, m.p. 112°, and -α-*phenyl*-γ-3 : 4-*dimethoxyphenyl*-, m.p. 122°, -α-*phenyl*-γ-p-*anisyl*-, m.p. 117°, -γ-*phenyl*-α-p-*anisyl*-, m.p. 115—117°, -αγ-*di*-p-*anisyl*-, m.p. 114°, and -αγ-*diphenyl-propylamine*, m.p. 88—89°, are similarly obtained. N-*Acetyl*-α-p-*anisylethylamine*, m.p. 74—75°, and the Ac, m.p. 91—92° (lit. 93—94°), *propionyl*, m.p. 79°, n-*butyryl*, m.p. 80—81°, and iso*valeryl* derivative, m.p. 104°, of 3 : 4 : 5 : 1-$(OMe)_3C_6H_2{\cdot}[CH_2]_2{\cdot}NH_2$ (mescaline) are described. 7-Nitro-4′-methoxystilbene is reduced (Zn dust, EtOH–AcOH) to the corresponding oxime, which with H_2–PtO_2–EtOH–$H_2C_2O_4$ gives α-phenyl-β-p-anisylethylamine (as *oxalate*, m.p. 197°; *Ac* derivative, m.p. 150°). 7-Nitro-3′ : 4′-di- and -3′ : 4′ : 5′-tri-methoxystilbene similarly afford α-phenyl-β-3 : 4-di- and -3 : 4 : 5-tri-methoxyphenylethylamine (*Ac* derivatives, m.p. 143—144° and 153—154°, respectively). *p*-$OMe{\cdot}C_6H_4{\cdot}CH_2{\cdot}NO_2$ and (**I**) in EtOH–NH_2Me give 7-*nitro*-4 : 3′ : 4′ : 5′-*tetramethoxystilbene*, m.p. 137°. H. B.

New preparation of hydroxy-aromatic ketone. I. Monoketones. S. S. Israelstam and H. Stephen. **II. Diketones.** S. S. Israelstam (*J. S. African Chem. Inst.*, 1943, **26**, 41—48, 49—53).—I. A trace of conc. H_2SO_4 is added to an equimol. mixture of Ac_2O and a phenol containing two or more OH groups in the *meta* position; there is an immediate rise in temp. of ~60°, after which the mixture is heated at 130° for 15 min.; the product is boiled with H_2SO_4–EtOH to hydrolyse any *O*-Ac derivative. Thus are obtained: 2 : 4 : 1-

$(OH)_2C_6H_3$·COMe, m.p. 146°; 2 : 4 : 1-$(OH)_2C_6H_3$·COEt, m.p. 99°; 2 : 4 : 1-$(OH)_2C_6H_3$·COPr^a, m.p. 69°, and its 4-Me, m.p. 32·5°, and 2-Me, m.p. 69°, ethers; 2 : 4 : 1-$(OH)_2C_6H_3$·COPh, m.p. 144°; 2 : 4 : 1-$(OH)_2C_6H_3$·CH_2Bz, m.p. 114—115°; 2 : 4 : 6 : 1-$(OH)_3C_6H_2$·COMe, m.p. 213—214°; 2 : 4 : 6 : 1-$(OH)_3C_6H_2$·COEt, m.p. 170—171°; 2 : 3 : 4 : 1-$(OH)_3C_6H_2$·COMe, m.p. 169—170; 2 : 3 : 4 : 1-$(OH)_3C_6H_2$·COEt, m.p. 126—127°; 2 : 6 : 4 : 1-$(OH)_2C_6H_2$Me·COMe, m.p. 146°; 2 : 6-*dihydroxy*-4-*methylpropiophenone* (+H_2O), m.p. 129° (6-*Me ether*, m.p. 75°); 2-*hydroxy*-6-*methoxy*-4-*methylacetophenone*, m.p. 81°; 2 : 4 : 6 : 1-$(OH)_2C_6H_2$Me·COEt, m.p. 122°. The "phloracetophenone" of Hoesch (A., 1915, i, 820) is the corresponding ketimine sulphate.

II. Increase in the relative proportions of acid anhydride and conc. H_2SO_4 results in the introduction of two acyl groups. Thus resorcinol affords a mixture of 2 : 4-, m.p. 92°, and 4 : 6-diacetylresorcinol, m.p. 182° (*Me_2 ether*, m.p. 171°); similar mixtures are obtained from resorcinol, AcCl, and conc. H_2SO_4 and from *m*-$C_6H_4(OAc)_2$ and hot conc. H_2SO_4. 4 : 6- and 2 : 4-Dipropionylresorcinol, m.p. 125° and 81°, respectively, are obtained similarly. All the following diketones give a red colour with $FeCl_3$ in EtOH: *diacetylphloroglucinol*, m.p. 153°; *dipropionylphloroglucinol*, m.p. 137—138°; 4 : 6-diacetylpyrogallol, m.p. 188° (diacetate, m.p. 218°); 4 : 6-*dipropionylpyrogallol*, m.p. 186°. H. W.

Biochemistry of the lower fungi. VI. Synthesis of fumigatin. T. Posternak and H. W. Ruelius (*Helv. Chim. Acta*, 1943, **26**, 2045—2049).—3 : 5 : 4 : 1-$(OH)_2C_6H_2$(OMe)·CHO is hydrogenated in abs. EtOH containing PtO_2 to 3 : 5-*dihydroxy*-4-*methoxybenzyl alcohol* (**I**), m.p. 177—178°, or in glacial AcOH containing Pd-black to 3 : 5-*dihydroxy*-4-*methoxytoluene* (**II**), m.p. 135—136°, also obtained under these conditions from (**I**). (**II**) is converted by amyl nitrite through the K salt into 2-*nitroso*-3 : 5-*dihydroxy*-4-*methoxytoluene*, m.p. 118° (decomp.), reduced catalytically or by $Na_2S_2O_4$ to the unstable amine which is immediately oxidised to fumigatin [3-hydroxy-4-methoxy-2 : 5-toluquinone], m.p. 113—113·5°. H. W.

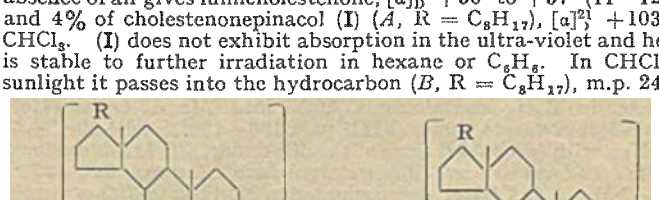
Biochemistry of the lower fungi. V. New syntheses of phœnicin and *iso*phœnicin. T. Posternak, H. W. Ruelius, and J. Tcherniak (*Helv. Chim. Acta*, 1943, **26**, 2031—2044).—4 : 1 : 3 : 5-NO_2·$C_6H_2Me(OH)_2$ is converted by Me_2SO_4 and NaOH into 4-*nitro*-3 : 5-*dimethoxytoluene*, m.p. 147—147·5°, reduced (H_2–PtO_2–abs. EtOH) to the 4-NH_2-compound, m.p. 64—65° (*H sulphate*), whence the 4-*I*-compound, m.p. 96—97°. This is transformed by activated Cu (Adams) at 170—210° into 2 : 6 : 2′ : 6′-*tetramethoxy*-4 : 4′-*dimethyldiphenyl*, m.p. 145—146°, which with HNO_3 (*d* 1·4) in Ac_2O at −10° affords 3 : 3′-*dinitro*-2 : 6 : 2′ : 6′-*tetramethoxy*-4 : 4-*dimethyldiphenyl*, m.p. 197—198°, reduced to the 3 : 3′-$(NH_2)_2$-compound, m.p. 168° or (+$2H_2O$) m.p. 132—134° (evolution of steam) and, after resolidification, m.p. 168°; this can be diazotised normally with production of relatively very stable salts. It is oxidised by $Na_2Cr_2O_7$ and H_2SO_4 to 2 : 2′-*dimethoxy*-4 : 4′-*dimethyldiphenyl*-3 : 6 : 3′ : 6′-*diquinone* (*phoenicin Me_2 ether*), m.p. 131—132°, identical with the compound obtained from phoenicin (**I**), Ag_2O, and MeI and hydrolysed to (**I**) by 2% Na_2CO_3 at 100°. 4-Iodotoluquinone is converted by Thiele's reagent at room temp. into a mixture of 4-iodo-2 : 3 : 5-(**II**), m.p. 154—155°, and 4-*iodo*-2 : 5 : 6-*triacetoxytoluene* (**III**), m.p. 117—118°, which retains a trace of (**II**). (**II**) is transformed by activated Cu into leucophœnicin hexa-acetate (**IV**), m.p. 200—201°. Leuco*iso*phœnicin hexa-acetate, m.p. 178—181°, is obtained similarly from (**III**) or better, together with (**IV**), from an equimol. mixture of (**II**) and (**III**). (**II**) is partly hydrolysed by HCl–MeOH to 4-*iodohydroxyuiacetoxytoluene* (**V**), m.p. 173—175°; partial hydrolysis followed by methylation (CH_2N_2) leads to 4-*iododiacetoxymethoxytoluene* (**VI**), m.p. 164° [also obtained by methylation (CH_2N_2 in Et_2O) of (**V**)], and 4-*iodoacetoxydimethoxytoluene*, m.p. 82—84°. (**VI**) is converted by activated Cu into *tetra-acetoxydimethoxy*-4 : 4′-*dimethyldiphenyl*, m.p. 171° (also an unstable form, m.p. 149°), which is converted by hydrolysis followed by oxidation by $FeCl_3$ into (**I**). Partial hydrolysis (HCl in abs. MeOH) of (**III**) gives 4-*iodohydroxydiacetoxytoluene*, m.p. 196—198°, transformed by CH_2N_2 into the corresponding *OMe*-compound, m.p. 111—113°. *Hexamethyl-leucophœnicin*, m.p. 123°, is obtained by treating leucophœnicin with Me_2SO_4 and NaOH in presence of $Na_2S_2O_4$. *Hexamethyl-leuco*iso*phœnicin*, m.p. 85—86°, is obtained analogously and is converted by HNO_3 (*d* 1·4) in Ac_2O at −10° into a $(NO_2)_2$-derivative, m.p. 154°. Leuco*iso*phœnicin is converted by boiling HBr (*d* 1·5) into *anhydroleucoiso*phœnicin, m.p. 290—291° (block). H. W.

IV.—STEROLS AND STEROID SAPOGENINS.

Oxidative degradation of neoergosteryl acetate. R. P. Jacobsen (*J. Amer. Chem. Soc.*, 1943, **65**, 1789—1792).—The acetate (**I**), m.p. 118—119°, of neoergosterol (modified prep. from bisergostatrienol in boiling *n*-C_5H_{11}·OH–N_2), m.p. 152·5—154° (lit. 151—152°), $[\alpha]_D^{19}$ −10° in $CHCl_3$, with successively OsO_4–Et_2O at room temp., aq. EtOH–Na_2SO_3, and HIO_4 in Et_2O containing a little MeOH at 15° gives α-3(β)-hydroxy-$\Delta^{5:7:9}$-œstratrien-17-ylpropionic acid (**II**), +0·5H_2O, m.p. 206·5—208·5° (Remesov, A., 1938, II, 18, m.p. 210—212°), $[\alpha]_D^{19}$ −7° in $COMe_2$ [*Me* ester (**III**), m.p. (air-dried) 173—175°, (dried at 110°/vac.) 174—176·5°], also obtained (m.p. 203·5—206°) from (**I**) by O_3 in 2 : 1 AcOH–CCl_4 in 6·5—9% yield (cf. *loc cit.*). With hot Ac_2O–C_5H_5N and then CH_2N_2, (**II**) gives its Me ester acetate (**IV**), m.p. 159·5—161·5° (*loc. cit.*, m.p. 144—145°). (**IV**) with MgPhBr–Et_2O–PhMe gives αα-*diphenyl*-β-3(β)-*acetoxy*-$\Delta^{5:7:9}$-œ*stratrien*-17-*yl*-n-*propyl alcohol*, +0·5H_2O, m.p. 112—120° (effervescence), dehydrated by Ac_2O–C_5H_5N and then boiling Ac_2O (a little)–AcOH to αα-*diphenyl*-β-3(β)-*acetoxy*-$\Delta^{5:7:9}$-œ*stratrien*-17-*yl*-Δ^a-*propene* (16%), m.p. 197—201°, $[\alpha]_D^{19}$ +171° in $CHCl_3$. With MgMeI in PhMe–Et_2O, (**III**) gives γ-3(β)-*hydroxy*-$\Delta^{5:7:9}$-œ*stratrien*-17-*yl*-β-*methyl*-n-*butan*-β-*ol* (**V**), m.p. 179—183°, $[\alpha]_D^{19}$ −27° in $CHCl_3$, which with Ac_2O–C_5H_5N at room temp. gives the 3(β)-*acetate*, m.p. 127—130°. This is dehydrated by AcOH + a little Ac_2O at 150—155° (less well, Ac_2O–$ZnCl_2$ or anhyd. $H_2C_2O_4$), to γ-3(β)-*acetoxy*-$\Delta^{5:7:9}$-œ*stratrien*-17-*yl*-β-*methyl*-Δ^a-n-*butene* (**VI**), m.p. 135—136°, $[\alpha]_D$ −14° in $CHCl_3$ [corresponding 3(β)-3′ : 5′-*dinitrobenzoate*, m.p. 252—255° (decomp.)]. With OsO_4– and then HIO_4–Et_2O, (**VI**) gives, after hydrolysis, α-3(β)-*hydroxy*-$\Delta^{5:7:9}$-œ*stratrien*-17-*ylethyl Me ketone*, m.p. 177—181°, $[\alpha]_D^{19}$ −22° in $CHCl_3$ (*acetate*, m.p. 148—152°), which with MgMeI–PhMe–Et_2O gives (**V**), thus proving the structure. M.p. are corr. R. S. C.

Steroid excretion in a case of adrenocortical carcinoma. I. Isolation of a Δ^5-androstene-3(β) : 16 : 17-triol. H. Hirschmann (*J. Biol. Chem.*, 1943, **150**, 363—379).—Urine obtained from a boy with adenocarcinoma of the adrenal cortex is hydrolysed by boiling with HCl; it is extracted with Et_2O and the 17-keto-steroids in the neutral fraction are determined (method: Callow *et al.*, A., 1938, III, 905). The neutral fraction is extracted with C_6H_6 and the insol. residue affords Δ^5-*androstene*-3(β) : 16 : 17-*triol* (**I**), $C_{19}H_{30}O_3$, m.p. 267—270° (decomp.). Ac_2O–C_5H_5N at room temp. gives the *triacetate* (**II**), m.p. 189·5—191°, $[\alpha]_D^{26}$ −102° in 95% EtOH; the mother-liquors (chromatographic separation) yield a *diacetate*, m.p. 183—187°, and 3-*monoacetate* (**III**), m.p. 243—245°, both of which are hydrolysed by aq. NaOH–MeOH at room temp. to (**I**), +0·5MeOH, m.p. 266—270° (decomp.). Hydrogenation (Pd–$CaCO_3$; EtOH) of (**I**) affords *androstane*-3(β) : 16 : 17-*triol* (**IV**), m.p. 256—260° (digitonide); its *triacetate*, m.p. 175·5—176·5°, $[\alpha]_D^{26}$ −44° in 95% EtOH, is obtained by hydrogenating (**II**). (**I**) and HIO_4,$2H_2O$–aq. dioxan (in N_2) at room temp. give a *product*, m.p. 131—134°. CrO_3–AcOH at room temp. (21 hr.) convert (**IV**) into 3-ketoæ*tio*allobilianic acid (**V**), m.p. 253—256°, which is also obtained from *iso*androsterone as follows: NaOMe–MeOH–PhCHO afford 16-*benzylideneandrostan*-3(β)-*ol*-17-*one*, m.p. 181·5—182·5°; its *acetate*, m.p. 237—238°, and CrO_3–AcOH at 60° yield β-3-hydroxy-æ*tio*allobilianic acid, new m.p. 254—257° (decomp.), converted by CrO_3–AcOH at room temp. into (**V**). (**III**) with successively Br–AcOH, CrO_3–AcOH at room temp., and $COMe_2$–NaI gives β-3-hydroxy-Δ^5-æ*tio*bilienic acid, forms, m.p. 232—236° and 247—255°, or after acetylation (Ac_2O–C_5H_5N), β-3-acetoxy-Δ^5-æ*tio*bilienic anhydride, m.p. 186—188°. (**I**) is not identical with that described by Butenandt *et al.* (A., 1939, II, 165) or Stodola *et al.* (A., 1942, II, 104), there being probably a different spatial arrangement at $C_{(14)}$ or $C_{(17)}$ (or both). (**I**) could not be extracted from the urine prior to hydrolysis. M.p. are corr. A. T. P.

Photochemical transformation of αβ-unsaturated steroid ketones under the influence of ultra-violet light. II. A. Butenandt and L. Poschmann (*Ber.*, 1940, **73**, [*B*], 893—897; cf. A., 1939, II, 328).—Exposure to ultra-violet light of cholestenone in pure hexane in absence of air gives lumicholestenone, $[\alpha]_D^{23}$ +36° to +37° (11—12%), and 4% of cholestenonepinacol (**I**) (*A*, R = C_8H_{17}), $[\alpha]_D^{21}$ +103° in $CHCl_3$. (**I**) does not exhibit absorption in the ultra-violet and hence is stable to further irradiation in hexane or C_6H_6. In $CHCl_3$ in sunlight it passes into the hydrocarbon (*B*, R = C_8H_{17}), m.p. 244—



(*A.*) (*B.*)

246° (block) (slight decomp. at 170°), $[\alpha]_D^{23}$ −230° in $CHCl_3$. The change is ascribed to the catalytic influence of HCl derived from decomp. of $CHCl_3$; it also occurs in EtOH or C_6H_6 containing a trace of HCl in absence of light. Analogously, testosterone propionate (**II**) in C_6H_6–hexane (1 : 10) affords lumitestosterone propionate (**II**), m.p. 350—355°, and the *pinacol* (*A*, R = O·COEt), m.p. 223° after softening, $[\alpha]_D^{23}$ +75° in $CHCl_3$, also obtained by reduction of (**II**) by Na–Hg in 96% EtOH and dehydrated by repeated dissolution in EtOH or insolation in $CHCl_3$ to the *compound* (*B*, R = O·COEt), m.p. 275—280°, decomp. >230°, $[\alpha]_D^{23}$ −272° in $CHCl_3$. H. W.

Barbier–Wieland degradation of 3-hydroxy-12-ketocholanic acid. B. Riegel and R. B. Moffett (*J. Amer. Chem. Soc.*, 1943,

65, 1971—1973).—Steric hindrance at the 12-CO allows application of the Barbier–Wieland degradation in the 3-hydroxy-12-ketocholanic acid series. A little AcCl in MeOH at the b.p. and then room temp. or $Pr^{\beta}OH$ at room temp. converts 3-hydroxy-12-ketocholanic acid into the Me (**I**), m.p. 111·5—113·5° (lit. 110—111·5°), or *Pr*$^{\beta}$ ester, m.p. 149·5—151°, respectively. With MgPhBr in boiling Et_2O–C_6H_6 and then, best, 7·5% KOH–MeOH, (**I**) gives *diphenyl-3-hydroxy-12-ketonorcholanylcarbinol* (**II**) (32%), m.p. 215—216·5°, converted by boiling Ac_2O–AcOH into *αα-diphenyl-β-12-keto-3-acetoxybisnorchanylethylene* (**III**), m.p. 180·5—182°, which with CrO_3–AcOH–$CHCl_3$ at ~35° and then boiling aq. NaOH gives 3-hydroxy-12-ketonorcholanic acid, m.p. 248—250° (Me ester, m.p. 149·5—151°). The crude H succinate, m.p. 97—115°, of diphenyl-3 : 12-dihydroxynorcholanylcarbinol (**IV**), m.p. 114—119°, with CrO_3–aq. AcOH at room temp. and then boiling KOH–MeOH gives (**II**), m.p. 214—215°., Ac_2O–AcOH and then 10% KOH–MeOH converts (**IV**) into *αα-diphenyl-β-3 : 12-dihydroxybisnorcholanylethylene*, +0·5MeOH (retained at 78°/1 mm.), m.p. 108—110°, which with $(CH_2{\cdot}CO)_2O$ in C_5H_5N at 100° (5 min.) and then room temp. (24 hr.) gives the 3-*H succinate*, m.p. 198—201°, converted by CrO_3–AcOH–H_2O at 0—5° and then boiling KOH–MeOH into *αα-diphenyl-β-3-hydroxy-12-ketobisnorcholanylethylene*, +0·5EtOH (retained at 78°/1 mm.), m.p. 158—159° [acetate = (**III**), m.p. 181·5—182·5°]. M.p. are corr. R. S. C.

Bile acids and related substances. XXVII. α-Oxides of the two 3-hydroxy- and the 3-keto-Δ^{11}-cholenic acid. G. H. Ott and T. Reichstein (*Helv. Chim. Acta*, 1943, **26**, 1799—1815).—Me 3-keto-Δ^{11}-cholenate (**I**) is hydrogenated (Raney Ni) in alkaline medium and then esterified (CH_2N_2) and acetylated to a mixture of Me 3(α)- (**II**), m.p. 119—121°, and Me 3(β)-acetoxy-Δ^{11}-cholenate (**III**), m.p. 149—151°, separated from one another by chromatography over Al_2O_3. Gradual addition of an aq. solution of NHBrAc and NaOAc,$3H_2O$ to (**II**) in $COMe_2$ at 55—30° and chromatography of the product over Al_2O_3 gives the corresponding dibromide, *Me* 11(α) : 12(α)-*oxido*-3(α)-*acetoxycholanate* (**III**), m.p. 154—155° $[\alpha]_D^{12}$ +62·0°±2° in $COMe_2$, and Me 12-keto-3(α)-acetoxy-Δ^9-cholenate (**V**), m.p. 146—148°, $[\alpha]_D^{14}$ +100·0°±2° in $COMe_2$. The formation of (**IV**) and possibly of (**V**) is due to the intervention of the Al_2O_3. Under somewhat modified conditions (**II**) is converted by NHBrAc in aq. $COMe_2$ containing NaOAc,$3H_2O$ or in C_5H_5N–C_6H_6 into *Me* 12-*bromo*-11(α)-*hydroxy*-3(α)-*acetoxycholanate* (**VI**), m.p. 201—203°, $[\alpha]_D^{17}$ +70·5°±2° in $COMe_2$. (**VI**) is unchanged by boiling C_5H_5N or by Al_2O_3 which has been washed with dil. HCl and hot MeOH and dried at 250° but converted into (**IV**) by Al_2O_3 in presence of a little C_5H_5N or by technical Al_2O_3 containing alkali. Zn dust and boiling AcOH or Zn–Cu in AcOH is without action on (**VI**). Hydrogenation at 50°/100—115 atm. in MeOH–C_5H_5N containing Raney Ni causes some formation of (**IV**). (**VI**) is oxidised by CrO_3 in AcOH–$CHCl_3$ to *Me* 12-*bromo*-11-*keto*-3(α)-*acetoxycholanate*, m.p. 183—185°, $[\alpha]_D^{15}$ +13·0°±2° in $COMe_2$, debrominated by Zn dust in warm AcOH to Me 11-keto-3(α)-acetoxycholanate, m.p. 131—133°. (**VI**) is transformed into (**IV**) by KOH–MeOH at room temp. followed by re-esterification (CH_2N_2), or by technical Al_2O_3 containing alkali. Short treatment with boiling AcOH leaves (**IV**) almost unchanged whereas longer treatment results in yellow, amorphous materials. CrO_3 in AcOH oxidises (**IV**) at room temp. to an unidentified neutral substance, m.p. 131—138°. Boiling H_2SO_4–MeOH followed by re-methylation and acetylation transforms (**IV**) into a product, m.p. 131—133°. (**IV**) is hydrogenated (120—145°/~150 atm.; Raney Ni–MeOH), then re-methylated and acetylated, to Me 11(α)-hydroxy-3(α)-acetoxycholanate, m.p. 147—149°. (**I**), NHBrAc, and NaOAc,$3H_2O$ in aq. $COMe_2$ afford *Me* 12-*bromo*-11(α)-*hydroxy*-3-*ketocholanate*, m.p. 166—167°, $[\alpha]_D^{18}$ +48·9°±2° in $COMe_2$, converted by technical Al_2O_3 containing alkali into Me 3-keto-11(α) : 12(α)-oxidocholanate (**VII**), m.p. 121—122°, $[\alpha]_D^{17}$ +34·0°+2° in $COMe_2$. (**III**) is converted by NHBrAc and NaOAc,$3H_2O$ in aq. $COMe_2$ or by NHBrAc in C_6H_6 containing C_5H_5N into *Me* 12-*bromo*-11(α)-*hydroxy*-3(β)-*acetoxycholanate* (**VIII**), m.p. 196—198°, $[\alpha]_D^{18}$ +50·4°±2° in $COMe_2$, with (probably) some of the dibromide. (**VIII**) is oxidised to *Me* 12-*bromo*-11-*keto*-3(β)-*acetoxycholanate*, m.p. 226—227°, $[\alpha]_D^{18}$ −7·3°±2° in $COMe_2$, debrominated to Me 11-keto-3(β)-acetoxycholanate, m.p. 174—175°. Technical Al_2O_3 transforms (**VIII**) into *Me* 11(α) : 12(α)-*oxido*-3(β)-*acetoxycholanate* (**IX**), m.p. 151—152°, $[\alpha]_D^{8}$ +39·9°±1° in $COMe_2$; the change is also conveniently effected by KOH–MeOH followed by methylation (CH_2N_2) and acetylation. (**IX**) is hydrolysed, esterified (CH_2N_2), and then oxidised to (**VII**), also obtained analogously from (**IV**). M.p. are corr. (block); limit of error ±2°. H. W.

Isomerisation of 17-hydroxy-20-keto-steroids. IV. Reaction of 3(β) : 17(α)-diacetoxy*allo*pregnan-20-one with magnesium methyl bromide. C. W. Shoppee and D. A. Prins (*Helv. Chim. Acta*, 1943, **26**, 2089—2095).—Addition of 3(β) : 17(α)-diacetoxy*allo*pregnan-20-one (**I**) in Et_2O-dioxan to MgMeBr in boiling Et_2O followed by treatment of the product with Ac_2O–C_5H_5N at room temp. gives unchanged material, small amounts of a substance, m.p. ~265°, 17(α) : 20-*dihydroxy*-3(β)-*acetoxy*-20-*methyl*allo*pregnane* (**II**), m.p. 168—170°, and 17*a*(β)-hydroxy-3(β)-acetoxy-17*a*-methyl-*D*-homo-androstan-17-one, m.p. 159—160°, $[\alpha]_D^{18}$ −33°±3° in $COMe_2$. Oxidation by (**II**) by CrO_3 in AcOH at room temp. and hydrolysis of the neutral portion of the product leads to *trans*-androsteronc, thus affording direct proof that (**I**) belongs to the *allo*pregnane series. M.p. are corr. (block); limits of error ~±2°. H. W.

Steroids and sex hormones. LXXXVII. *allo*Pregnan-3(β)-ol-21-al-20-one and pregnan-3(β)-ol-21-al-20-one. Testalolone. L. Ruzicka, V. Prelog, and P. Wieland (*Helv. Chim. Acta*, 1943, **26**, 2050—2057).—3(β)-Acetoxyætio*allo*cholanic acid is converted through the acid chloride and diazo-ketone into 21-chloro*allo*pregnan-3(β)-ol-20-one, m.p. 152—153°, which with hot C_5H_5N gives the *pyridinium* salt, $C_{26}H_{40}O_3NCl$, m.p. 273—274° (decomp.) (also +1H$_2$O), converted by *p*-NO·C_6H_4·NMe_2 into the nitrone, m.p. (indef.) 119—120°, which is hydrolysed by HCl to allo*pregnan*-3(β)-*ol*-21-*al*-20-*one* (**I**) [*monohydrate*, m.p. 155°, softens at 136°, $[\alpha]_D$ +92·7°±3° in C_5H_5N, giving after desiccation at 90°/high vac. a *semihydrate*, $[\alpha]_D$ +87·5°±3° in C_5H_5N; *dioxime*, m.p. 246—249° (decomp.); *Me*$_2$ *acetal*, m.p. 113—115°, $[\alpha]_D$ +111·5°±3° in $CHCl_3$]. Similarly 3(β)-acetoxyætiocholanic acid is converted into 21-*chloro*-*pregnan*-3(β)-*ol*-20-*one*, m.p. 184—185°, $[\alpha]_D$ +116·5°±2° in $CHCl_3$, transformed through the *pyridinium chloride*, m.p. 284° (decomp.), into *pregnan*-3(β)-*ol*-21-*al*-20-*one* (**II**) [*monohydrate*, m.p. ~143°, softens at 127°, $[\alpha]_D$ +103°±3° in C_5H_5N; *semihydrate*, m.p. 129—147° $[\alpha]_D$ +103°±3° in C_5H_5N; *dioxime*, m.p. 217—223° (decomp.); *Me*$_2$ *acetal*, m.p. 126—129°, $[\alpha]_D$ +132°±10° in $CHCl_3$]. (**I**) and (**II**) are oxidised by HIO_4 to 3(β)-hydroxyætio*allo*-, m.p. 245—247°, and 3(β)-hydroxyætio-cholanic acid, m.p. 224—225·5°, respectively and by CrO_3 in AcOH to the corresponding keto-acids. Neither (**I**) nor (**II**) is identical with testalolone (A., 1936, II, 644). M.p. are corr. H. W.

Pyridazine derivative of cholestanedione. K. Bursian (*Ber.*, 1940, **73**, [*B*], 922—923).—Contrary to Noller (A., 1940, II, 18) the pyridazine derivative (**I**) of cholestanedione is a well-defined cryst. compound. It has m.p. >200° to a brown liquid, softens and darkens at 170°. The vals. for the mol. wt. in $C_{10}H_8$, C_6H_6, PhOH, and exaltone do not reach the high data recorded by Noller but show ill-defined association varying from solvent to solvent and never indicating double the expected formula so that only the formula $C_{27}H_{44}N_2$ is possible. Solutions of (**I**) in boiling C_6H_6 are turned brown by passage of air whereas (**I**) can be subjected to protracted heating in a high vac. at ~180° without suffering change; at ~200° it melts to a brown liquid which does not form a sublimate. H. W.

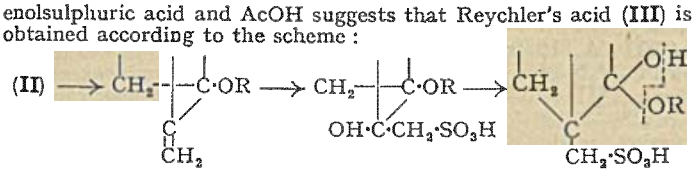
V.—TERPENES AND TRITERPENOID SAPOGENINS.

Condensation of dipentene dihydrochloride with phenol. A. Zinke and H. Hönel [with O. Benndorf, R. Dreweny, and E. Ziegler] (*J. pr. Chem.*, 1940, [ii], **156**, 97—102).—Dipentene dihydrochloride (**I**), PhOH, and a little $AlCl_3$ or $ZnCl_2$ at 40—65° give a resinous product from which CH_2Cl_2 or C_6H_6 extracts 1 : 8-*di*-p-*hydroxyphenylmenthane* (+H_2O) (**II**), m.p. 166° (*diacetate*, m.p. 122°; *dibenzoate*, m.p. 169·7°; *di*-p-*bromobenzoate*, m.p. 208·8°), which does not resinify when heated, could not be dehydrogenated, and is oxidised by HNO_3 (*d* 1·1) at 150° to picric acid. Halogenation of (**II**) gives no cryst. products. Resinous products are obtained from (**I**) and resorcinol or guaiacol; C_6H_6–$AlCl_3$ gives resin and some 1 : 8-*diphenylmenthane*, m.p. 242·5°. H. B.

Syntheses in the pinane series. G. Komppa (5 *Nordiske Kemikermode*, 1939, 213—214).—The total synthesis of α- (**I**) and δ-pinene (**II**), starting from R$(CO_2H)_2$ (**III**) (R = –CH<$^{CH_2}_{CMe_2}$>CH–), has been accomplished in the following stages: (**III**) via the anhydride and Me H ester gave CO_2Me·R·COCl, and thence, with ZnMeI, CO_2Me·R·COMe, and then (Reformatsky) CO_2Me·R·CMe(OH)·CH_2·CO_2Me (**IV**). H_2O was split off from (**IV**) with $SOCl_2$ to give CO_2Me·R·CMe:CH·CO_2Me, catalytically hydrogenated to CO_2H·R·CHMe·CH_2·CO_2H, the Pb salt of which on dry distillation gave verbanone (**V**). Reduction of (**V**) (Na–EtOH) gave C_8H_{14}<$^{CH\cdot OH}_{CH_2}$ which with $SOCl_2$–C_5H_5N gave (**II**). (**V**) with $NaNH_2$–CO_2 gave C_8H_{14}<$^{CO}_{CH\cdot CO_2H}$ which was electrolytically reduced to C_8H_{14}<$^{CH\cdot OH}_{CH\cdot CO_2H}$, losing H_2O (Ac_2O) to yield C_8H_{14}<$^{CH}_{C\cdot CO_2H}$ and thence (Curtius) C_8H_{14}<$^{CH_2}_{CO}$, converted into (**I**) by known methods. (Cf. A., 1942, II, 147.) M. H. M. A.

Mechanism of the sulphonation of camphor. P. Lipp and H. Knapp (*Ber.*, 1940, **73**, [*B*], 915—921).—The (incorrect) hypothesis that the by-product (**I**) obtained by Frèrejacque (A., 1926, 1251) in the sulphonation of camphor (**II**) is a mixed anhydride of camphor-

enolsulphuric acid and AcOH suggests that Reychler's acid (**III**) is obtained according to the scheme :



(R — H, Ac, or SO_3H). In support of this hypothesis it is shown that (**III**) is obtained from 1-hydroxycamphene (**IV**) and Ac_2O–H_2SO_4 more rapidly than from (**II**). (**I**) yields AcOH but no trace of H_2SO_4 under the influence of $Ba(OH)_2$ and hence is an acetate but not a H sulphate. Further it is resistant to $KMnO_4$ in $COMe_2$, does not absorb Br in $CHCl_3$, and cannot be catalytically hydrogenated; it is therefore saturated and is not an intermediate compound in the sulphonation of (**II**). The *tert.* nature of OH in (**IV**) is established by the positive Wienhaus reaction and by the resistance of (**IV**) to the formation of a *p*-nitrobenzoate. Attempts to establish the presence of the semicyclic ethylenic linking in (**IV**) by fission with O_3 to CHO_2 and hydroxycamphenilone show that ketonisation to (**II**) takes place more rapidly than ozonisation. It is, however, readily hydrogenated giving 1-*hydroxyisocamphane* (**V**), m.p. 113·5—114°. Attempted methylation of (**V**) with Ag_2O and MeI leads to (**II**), the Ag_2O behaving as a dehydrogenating agent. (**V**) has the constitution assigned by Kresstinski *et al.* (A., 1937, II, 253) to their *iso*borneol. Since (**V**) has quite different properties from those of *iso*borneol, the observations of Kresstinski must be explained otherwise. H. W.

Triterpene resinols and related acids. XIV. Oxidation of acetylursolic acid. E. S. Ewen and F. S. Spring (*J.C.S.*, 1943, 523—525). —Oxidation (AcOH–H_2CrO_4) of acetylursolic acid affords *ketoacetylursolic acid* (**I**), $C_{32}H_{48}O_5$, m.p. 315—316° (decomp.), $[\alpha]_D^{20}$ +40·8° in $CHCl_3$, and a small amount of a *lactone*, $C_{32}H_{46}O_6$, m.p. 305—306° (decomp.). Similar oxidation of Et acetylursolate yields *Et ketoacetylursolate*, m.p. 210—212°, $[\alpha]_D^0$ +92° in $CHCl_3$, identical with that obtained from the acid and $CHMeN_2$. Quinoline and (**I**) give *nor-α-amyradienonyl acetate*, m.p. 203—205°, $[\alpha]_D^1$ +41° in $CHCl_3$, with loss of HCO_2H. This acetate contains the chromophoric system O:C·C:C·C:C. These transformations indicate that the CO_2H of ursolic acid is in the vicinity of the ethylenic linking.[4] F. R. S.

VI.—HETEROCYCLIC.

Synthesis of 2-keto*cyclo*hexylsuccinic acid and related substances. III. Syntheses involving ethylene and propylene oxides. J. A. McRae, E. H. Charlesworth, F. R. Archibald, and D. S. Alexander (*Canad. J. Res.*, 1943, **21**, B, 186—193).—Addition of $(CH_2)_2O$ to a well-cooled solution of $CHNa(CO_2Et)_2$ in EtOH followed by $CH_2Cl·CO_2Et$ and alkaline hydrolysis of the product gives 2-*keto-tetrahydrofuran-3-carboxylic-3-acetic acid*, m.p. 165° (*Et*$_2$ ester, b.p. 204—206°/15 mm.), which passes at 160° into 2-*ketotetrahydrofuran-3-acetic acid*, m.p. 56—58°; this is converted by NH_3–EtOH at 100° into *β-hydroxyethylsuccindiamide*, m.p. 137—139° (decomp.). Under similar conditions $Br·[CH_2]_2·CO_2Et$ affords *Et*$_2$ 2-*ketotetrahydrofuran-3-carboxylate-3-propionate*, b.p. 204—206°/15 mm.; the corresponding dicarboxylic *acid*, m.p. 125° (decomp.), is decarboxylated at 160° to 2-*ketotetrahydrofuran-3-β-propionic acid*, m.p. 51·5—53°. Analogously CH_2PhCl gives *Et* 2-*keto-3-benzyltetrahydrofuran-3-carboxylate*, b.p. 195—197°/0·5 mm., hydrolysed and then decarboxylated to 2-*keto-3-benzyltetrahydrofuran*, b.p. 165—166°/10 mm. Condensation of propylene oxide (**I**) with $CHNa(CO_2Et)_2$ and hydrolysis of the product leads to the unstable β-hydroxypropylmalonic acid (isolated as the *Ba* salt), decarboxylated at 160° to 2-keto-5-methyltetrahydrofuran [γ-valerolactone], b.p. 83—84°/12 mm.; if the Na derivative of the original condensation product is not hydrolysed by NaOH but immediately acidified the unstable γ-hydroxy-α-carbethoxyvalerolactone, b.p. 125—135°/25—40 mm. (partial decomp.), results. Successive treatments of $CHNa(CO_2Et)_2$ in EtOH with (**I**) and $Br·[CH_2]_2·CO_2Et$ followed by hydrolysis and decarboxylation of the product lead to 2-*keto-5-methyltetrahydrofuran-3-β-propionic acid*, m.p. 54—56°. H. W.

New furancarboxylic acids from glucose. T. Széki and E. László (*Ber.*, 1940, **73**, [*B*] 924—929).—Glucose, $CH_2Bz·CO_2Et$, and $ZnCl_2$ in abs. EtOH give *Et* 2-*phenyl-5-αβγδ-tetrahydroxybutylfuran-3-carboxylate* (**I**), m.p. 176—177°, $[\alpha]_D$ −38·4° in AcOH, converted by Ac_2O and C_5H_5N at 0° into the *tetra-acetate*, m.p. 95°, $[\alpha]_D^6$ −51·2° in $CHCl_3$, and by benzoylation into an oil. Oxidation of (**I**) by $Pb(OAc)_4$ in AcOH–C_6H_6 at 0° affords *Et 5-aldehydo-2-phenylfuran-3-carboxylate* (**II**), m.p. 76°, $[\alpha]_D$ ±0° (*semicarbazone*, m.p. 170—171°; *phenylhydrazone*, m.p. 124—126°), which gives a cryst. additive product with $NaHSO_3$. (**II**) is converted by boiling 15% NaOH containing Ag_2O into 2-*phenylfuran-3-5-dicarboxylic acid*, m.p. 270—271° (decomp.) (*dichloride*, m.p. 68—72°; *dianide*, m.p. 206—208°; *dianilide*, m.p. 147—150°; *Me*$_2$ ester, m.p. 95—96°). *2-Phenyl-5-tetrahydroxybutylfuran-3-carboxylic acid*, m.p. 195—197° (decomp.), $[\alpha]_D^{23}$ −24·6° in AcOH, is oxidised [$Pb(OAc)_4$ in C_6H_6–AcOH] to *5-aldehydo-2-phenylfuran-3-carboxylic acid*, m.p. 145—147°, in poor yield. Similarly $CO(CH_2·CO_2Et)_2$ is condensed to *Et*$_2$ *5-tetrahydroxybutylfuran-3-carboxylate-2-acetate* (**III**), m.p. 128—130°, $[\alpha]_D^{20}$ −14·7° in MeOH, oxidised to *Et*$_2$ *5-aldehydofuran-3-carboxylate-2-acetate*, an oil (*semicarbazone*, m.p. 180—182°; *phenylhydrazone*, m.p. 96—97°; 3 : 5-*dinitrophenylhydrazone*, m.p. 168—170°). (**III**) is transformed by boiling alkaline $KMnO_4$ followed by MeOH into *Me*$_3$ *furan-2 : 3 : 5-tricarboxylate*, m.p. 68—73°. H. W.

Polyalkylbenzenes. XXXIII. 3 : 5 : 6-Trimethylcoumaran-2-one and its conversion into 4-hydroxy-3 : 5 : 6-trimethyl-1-*iso*propylcoumaran. L. I. Smith, J. A. King, W. I. Guss, and J. Nichols (*J. Amer. Chem. Soc.*, 1943, **65**, 1594—1599; cf. A., 1943, II, 193).—2 : 3 : 5 : 1-$C_6H_2Me_3·O·CH_2·CO_2H$ (prep. from 2 : 3 : 5 : 1-$C_6H_2Me_3·OH$ by K_2CO_3–$CH_2Br·CO_2Et$–$COMe_2$ and then NaOEt–EtOH), m.p. 130—131° (lit. 128°), in H_2SO_4 at 90—95° gives 3 : 5 : 6-*trimethylcoumaran-2-one* (**I**) (86%), m.p. 90·5—91·5° [2 : 4-*dinitrophenylhydrazine* salt, m.p. 231° (decomp.), of the enolic form], converted by $ZnCl_2$–EtOH exothermally into 2-*ethoxy*-3 : 5 : 6-*trimethylcoumarone*, m.p. 86—88°. With a drop of H_2SO_4 in Ac_2O, (**I**) gives 2-*acetoxy*-3 : 5 : 6-*trimethylcoumarone*, m.p. 88—89°, which with Br–CCl_4 gives 2-*acetoxy*-3 : 5 : 6-*trimethylcoumaran-1-one*, m.p. 127·5—128·5°. With $ZnCl_2$ in boiling $COMe_2$, (**I**) gives 3 : 5 : 6-*trimethyl-1-isopropylidenecoumaran-2-one* (**II**), m.p. 90·5—91·5°, reduced by H_2–Raney Ni in EtOH at 200°/3000 lb. to 3 : 5 : 6-*trimethyl-1-isopropylcoumaran* (**III**), m.p. 38—39°, and converted by O_3 in EtBr and then H_2O_2–H_2O into 2-*hydroxy*-3 : 4 : 6-*trimethylbenzoic acid*, m.p. 181—182° (decomp.) (decarboxylated at > m.p. to 2 : 3 : 5 : 1-$C_6H_2Me_3·OH$). 2 : 3 : 4 : 5 : 1-$OH·C_6HMe_3·CO_2H$, m.p. 181° (decomp.), is obtained from 2 : 4 : 5 : 1-$C_6H_2Me_3·ONa$ and (solid) CO_2 at 250°. With Br–CCl_4, (**II**) gives HBr and 1-*bromo*-3 : 5 : 6-*trimethyl-1-α-bromoisopropylcoumaran*, m.p. 127—128° (decomp.). Br–CCl_4 converts (**III**) into 4-*bromo*-3 : 5 : 6-*trimethyl-1-isopropylcoumaran*, m.p. 65—66°, which with *cyclo*hexyl bromide and EtBr and then Mg in Et_2O gives a Mg derivative, whence O_2 yields 4-hydroxy-3 : 5 : 6-trimethyl-1-*iso*propylcoumaran, m.p. 119° (acetate, m.p. 76—77°) (cf. A., 1943, II, 240). Adding Na and then 1 : 2 : 3 : 5 : 4-O:C_6HMe_3:O to $CH_2(COPr^a)_2$ (prep. from Pr^aCO_2Et and $COMePr^a$ by way of the Cu derivative, m.p. 145—150°), b.p. 85—86°/11 mm., in EtOH gives 4-*hydroxy*-3 : 5 : 6-*trimethyl*-1-n-*propylcoumarone* (16%), m.p. 88—89°, reduced by H_2–Raney Ni in EtOH at 135°/1300 lb. to the derived *coumaran*, m.p. 96—97°. R. S. C.

Reaction between quinones and metallic enolates. XVII. Dibromo-*p*-xyloquinone and sodiomalonic ester. L. I. Smith and J. Nichols (*J. Amer. Chem. Soc.*, 1943, **65**, 1739—1747; cf. A., 1942, II, 267).—1 : 2 : 5 : 4-O:$C_6H_2Me_2$:O (**I**) or 2 : 5 : 1 : 4-$C_6H_2Me_2(OH)_2$ (**II**), m.p. 208—213° (lit. 208° to 213°), with Br in AcOH at room temp. gives the red dibromoquinhydrone, converted by HNO_3 in hot EtOH into 1 : 2 : 5 : 3 : 6 : 4-O:$C_6Me_2Br_2$:O (**III**), softens 178°, m.p. 183—184° (derived quinol, m.p. 174·5—175·5° after softening), which with $CHNa(CO_2Et)_2$ (2 mols.) in pure dioxan at room temp. gives *Et*$_2$ 5-*bromo*-3 : 6-*dimethyl*-1 : 4-*benzoquinon-2-ylmalonate* (**IV**) (83·7%; much less under other conditions), m.p. 65—66°. With $Na_2S_2O_4$–H_2O–Et_2O or H_2–PtO_2 in light petroleum this gives the derived *quinol* (**V**), softens 108°, m.p. 111—112°, which with H_2SO_4 (2 drops) in Ac_2O at room temp. gives *Et*$_2$ 6-*bromo*-2 : 5-*diacetoxy*-p-3-*xylylmalonate* (**VI**), m.p. 110—111°, and, when shaken in $CHCl_3$ with 75% H_2SO_4, is cyclised to give *Et* 5-*bromo*-4-*hydroxy*-3 : 6-*dimethylcoumaran-1-one-2-carboxylate* (**VII**) (91·2%), m.p. 117—118·5° [*acetate* (**VIII**), m.p. 120—122°]. Boiling (**IV**) with Zn in AcOH, (**VII**) in AcOH, or (**VIII**) in 1 : 1 HCl–AcOH gives 5-*bromo*-4-*hydroxy*-3 : 6-*dimethylcoumaran-1-one* (**IX**), m.p. 200—201° (decomp.) [*acetate*, m.p. 166—168°, obtained from (**IX**) by Ac_2O–H_2SO_4 at room temp. or (**VIII**) by boiling AcOH]. Me_2SO_4–KOH converts (**V**) in boiling MeOH into *Et* 5-*bromo*-4-*methoxy*-3 : 6-*dimethylcoumaran-1-one-2-carboxylate* (**X**), m.p. 96—97°, with some 5-*bromo*-1 : 4-*dimethoxy*-3 : 6-*dimethylbenzfuran-2-carboxylic acid* (**XI**), m.p. 210—211° (bath preheated at 200°) (decomp.), both [(50·8% of (**X**)] also obtained from (**VII**) by NaOH–Me_2SO_4 and both converted by boiling 70% AcOH into 5-*bromo*-4-*methoxy*-3 : 6-*dimethylcoumaran-1-one* (**XII**), m.p. 165—166°, unchanged by boiling KOH–EtOH–H_2O. With KOH–Me_2SO_4 in boiling MeOH, (**IX**) (81·7% yield) or (**XII**) (62·7% yield) gives 5-*bromo*-3 : 6-*dimethoxy*-p-2-*xylylacetic acid* (**XIII**), m.p. 158—159°. Me_2SO_4–KOH converts (**II**) in boiling MeOH into 2 : 5 : 1 : 4-$C_6H_2Me_2(OMe)_2$ (**XIV**), m.p. 107—108°, which with Br–AcOH gives 3-*bromo*-2 : 5-*dimethoxy*-p-*xylene* (75·8%), m.p. 57—59°, purified by chromatography and converted by HCl–CH_2O–AcOH at 60—70° into 4-*bromo*-3 : 6-*dimethoxy*-2 : 5-*dimethylbenzyl chloride* (77·8%), m.p. 94—98°, which with boiling KCN–EtOH–H_2O gives the *cyanide*, m.p. 115—116°, hydrolysed by boiling H_2SO_4–AcOH–H_2O to (**XIII**). With an excess of $CHNa(CO_2Et)_2$ in pure dioxan, (**IV**) gives 2 : 5-*dimethyl*-3 : 6-*bisdicarbethoxymethyl*-p-*benzoquinone* (**XV**) (15·7%), m.p. 74—76°, not obtained directly from (**III**) and reduced by aq. $Na_2S_2O_4$–Et_2O to the *quinol* (80%), m.p. 151—154°, which, when shaken in $CHCl_3$ with 75% H_2SO_4, gives 2 : 6-*diketo*-3 : 7-*dicarbethoxy*-4 : 8-*dimethylbenz*[1, 2-b-4 : 5-b′-]*tetrahydrodifuran* [*bis*-1′-*keto*-2′-*carbethoxy*-1′ : 2′-*dihydrofurano*-1′ : 2′-2 : 3-1″ : 2″ : 5 : 6-p-*xylene*] (**XVI**) (62·5%), m.p. 129—131°. In boiling 80% AcOH, (**XVI**) gives 2 : 6-*diketo*-4 : 8-*dimethylbenz*[1,2-b-4 : 5-b′-]*tetrahydrodifuran* [*bis*-1′-*keto*-1′ : 2′-*dihydrofurano*-1′ : 2′-2 : 3-1″ : 2″-5 : 6-p-*xylene*], decomp. 337—340°, also obtained from (**XV**) by Zn in boiling 70% AcOH and

converted by KOH–Me_2SO_4–MeOH into 2 : 5-*dimethoxy*-p-*xylylene*-3 : 6-*diacetic acid* (**XVII**) (34·6%), m.p. 267—271° (decomp.). HCl–CH_2O converts (**XIV**) into 2 : 5-*dimethoxy*-3 : 6-*di*(*chloromethyl*)-p-*xylene* (89%), m.p. 165·5—166°, which with NaCN in EtOH–$COMe_2$ gives the *dinitrile*, m.p. 207—207·5°, and thence (H_2SO_4–AcOH–H_2O) (**XVII**). With an excess of $CHNa(CO_2Et)_2$ in pure dioxan, (**I**) gives Et 4-hydroxy-3 : 6-dimethylcoumaran-1-one-2-carboxylate [and 3·8% of (**XVI**)], which is hydrolysed and decarboxylated by distillation in steam to give 4-*hydroxy*-3 : 6-*dimethylcoumaran*-1-*one* (41·5%), m.p. 214—216°. R. S. C.

Crystalline natural α- and γ-tocopherols. C. D. Robeson (*J. Amer. Chem. Soc.*, 1943, **65**, 1660).—Natural α-, m.p. 2·5—3·5° ($E^{\circ}_{1\,cm.}$ 71 at 292 mμ.) and γ-, m.p. −3° to −2° ($E^{1\%}_{1\,cm.}$ 93·2 at 298 mμ.), and synthetic α-tocopherol, m.p. ~0° ($E^{1\%}_{1\,cm.}$ 70 at 292 mμ.), are prepared. Synthetic *dl*-α-tocopherol was amorphous. R. S. C.

Derivatives of 2- and 2 : 8-substituted dibenzfurans. H. B. Willis (*Iowa State Coll. J. Sci.*, 1943, **18**, 98—101).—Dibenzfuran derivatives are discussed. New m.p. are recorded for 2-benzoyldibenzfuran (135—136°) and its oxime (182—183°). The following are stated to be new but no analyses are given: di-(2-, m.p. 201—202° and di-(3-dibenzfuryl), m.p. 245—246°: dibenzfuran-2-carboxyldiethylamide, m.p. 77—78°, and -4-carboxyldimethylamide, m.p. 116·5°, 2-benzoyldibenzfuran-*x*-carboxylic acid, m.p. 265—266° (Me ester, m.p. 189—190°), 3-nitro-2 : 8-diamino-, m.p. 210—213° (Ac_2 derivative, m.p. 322—324°), -2-β-benzamidoethyl-, m.p. 183·5—183·9°, 3-sulphanilamido- (**I**), m.p. 245° (Ac derivative, m.p. 223—224°), 4-sulphanilamido- (**II**), m.p. 195° (Ac derivative, m.p. 218°), 1 : 9(?)-bisbenzeneazo-2 : 8-dihydroxy-dibenzfuran, m.p. 155—156°; Et_2 4-, m.p. 75—76°, and Et_2 3-aminodibenzfuran-*N*-ethylmalonate, m.p. 99—100°; 2-acetoxy-1-dibenzfurancarboxylic acid, m.p. 151—152°. (**I**) and (**II**) are too insol. to be tested pharmacologically. F. R. G.

Santonin series. I. Two new desmotroposantonins and two new desmotroposantanous acids. H. Minlon, C. P. Lo, and L. J. Y. Chu (*J. Amer. Chem. Soc.*, 1943, **65**, 1780—1781).—Santonin with a drop of H_2SO_4 in cold or warm Ac_2O gives *l*-desmotroposantonin (~100%), m.p. 194—195°. *d-iso*Desmotroposantonin in dil. H_2SO_4 at 100° gives l-*desmotroposantonin* (**I**), m.p. 260—261°, $[\alpha]_D^0$ −106·2°, which with the *d*-isomeride gives the dl-*compound* (**II**), m.p. 231—232° (*acetate*, m.p. 182—183°). Zn in dil. AcOH reduces (**I**) to d-*desmotroposantanous acid*, m.p. 175—176°, $[\alpha]^{21}$ +54·0°, which with the *l*- gives the dl-*acid*, m.p. 180—181°, also obtained by reducing (**II**). Alkali-fusion converts (**I**) into the low-melting *l*-desmotroposantonin. Nomenclature of the series is revised. R. S. C.

Halogenated *m*-dioxans.—See B., 1944, II, 6.

Synthesis of a tetrahydrothiophen with substituted amino-groups in the 2- and 5-positions. G. B. Brown and G. W. Kilmer (*J. Amer. Chem. Soc.*, 1943, **65**, 1674—1675).—*cis*-Tetrahydrothiophen-2 : 5-dicarboxylic acid [prep. from *meso*-$(CH_2{\cdot}CHBr{\cdot}CO_2H)_2$], sinters 135°, m.p. 141—143° (lit. 144—145°), gives the Et_2 ester, b.p. 157°/10 mm., converted by N_2H_4,H_2O in EtOH at ~70° into the *dihydrazide* (23%), m.p. 208—209°, which with $NaNO_2$–H_2O–HCl–Et_2O at 0° and then abs. EtOH at ~50° to the b.p. gives 2 : 5-*di*-(*carbethoxyamino*)*tetrahydrothiophen* (53%), m.p. 152—154°. In boiling N-HCl it gives much H_2S and in boiling 5% $Ba(OH)_2$ or NaOH gives 0·8 mol. of NH_3 in 30 min.; with HCl–EtOH–H_2O it gives $(CH_2{\cdot}CHO)_2$, isolated as di-*p*-nitrophenylhydrazone. R. S. C.

Relative reactivities of organometallic compounds. LI. Metallation of thianthren and dibenzo-*p*-dioxin. H. Gilman and C. G. Stuckwisch (*J. Amer. Chem. Soc.*, 1943, **65**, 1461—1464; cf. A., 1943, II, 293).—Thianthren (**I**) with $LiBu^a$ (improved prep.) in Et_2O and then solid CO_2 etc. gives *thianthren*-1-*carboxylic acid*, m.p. 217—218° [by decarboxylation gives (**I**)]. *o*-$C_6H_4Br{\cdot}SK$ with PhI and Cu-bronze in boiling xylene gives *o*-$C_6H_4Br{\cdot}SPh$ (65%), b.p. 203°/6 mm., converted by S and $AlCl_3$ into 1-*bromothianthren* (25%), m.p. 145°, which with $LiBu^a$ etc. gives (**I**) (proof of structure). With $LiBu^a$ and then $NH_2{\cdot}OMe$–Et_2O, (**I**) gives 1-*thianthrenylamine* (**II**), m.p. 139° [hydrochloride, m.p. 231° (decomp.)], which yields the N^4-*acetylsulphanilyl*, m.p. 154°, and thence the *sulphanilyl* derivative, decomp. >120°. 2-Aminothianthren yields the N^4-*acetylsulphanilyl*, m.p. 163°, and *sulphanilyl* derivative, decomp. >125°. 4-N^4-*Acetylsulphanilyl*-, m.p. 192°, amd 4-*sulphanilyl*-*amidophenoxthionin*, m.p. 168°, are also prepared. No BuSH, Bu_2S, or Bu_2S_4 is obtained from (**I**) and $LiBu^a$ if S is entirely removed from the (**I**), *e.g.*, by conc. NaOH (cf. A., 1939, II, 131; 1941, II, 54). Dibenzo-*p*-dioxin with $LiBu^a$–Et_2O gives, after carboxylation, *dicarboxylic acids*, m.p. 297—298° (20%; Me_2 ester, m.p. 142—143°) and >335° (7%; Me_2 ester, m.p. 202—204°); LiMe leads to *dibenzo-p-dioxin*-1-*carboxylic acid* (10%), m.p. 210° (*Me* ester, m.p. 86°). *Me* 3-*bromosalicylate*, m.p. 62°, could not be converted into dibenzo-*p*-dioxin-1 : 6-dicarboxylic acid. R. S. C.

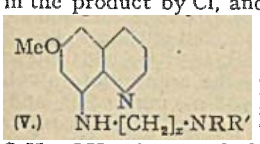
Heteropolar (XXXVI), polyarylated [compounds]. XII. Action of nitrosoaryl compounds on cyclones. Preparation of pentaphenylpyrrole. W. Dilthey, G. Hurtig, and H. Passing (*J. pr. Chem.*, 1940, [ii], **156**, 27—37).—Tetracyclone [2 : 3 : 4 : 5-tetraphenylcyclopentadienone] (**I**) reacts similarly to, but less vigorously than, phencyclone [2 : 5-diphenyl-3 : 4-2′ : 2″-diphenylene*cyclo*pentadienone] (**II**) (A., 1939, II, 326). *p*-$NO{\cdot}C_6H_4{\cdot}NMe_2$ and (**I**) in warm (not cold) C_5H_5N give 3 : 4 : 5 : 6-*tetraphenyl*-2-p-*dimethylaminophenyliso*-*oxazine* (**III**) (81—83%), m.p. 212—213° [colourless *monoperchlorate*, m.p. 239—240° (decomp.); *picrate*, m.p. 167—169° (decomp.); no reaction with MgMeI], and CO (83%). *cis*-$(CPhBz{\cdot})_2$ and *p*-$NH_2{\cdot}C_6H_4{\cdot}NMe_2$,HCl in boiling C_5H_5N–N_2 give (**III**) and impure 2 : 3 : 4 : 5-*tetraphenyl*-1-p-*dimethylaminopyrrole*, m.p. 270—273°. PhNO and (**II**), alone at 70°, or exothermally in C_5H_5N, give (i) CO (61·3%) and 9 : 10-*dibenzoylphenanthrenemonoanil* (**IV**) (57—59%), m.p. 217—218° [*perchlorate*, m.p. 297—298° (decomp.); *picrate*, m.p. 227° (decomp.)], and (ii) CO_2 (25·2%) and 1 : 2 : 5-*triphenyl*-3 : 4-*diphenylenepyrrole* (**V**) (23—25%), m.p. 351° (no salts or reaction with MgMeI). 2 : 5-Diphenyl-3 : 4-diphenylenefuran, NH_2Ph,HCl, and Al_2O_3 at 400° give (**V**). 50—70% of (**V**) is obtained by boiling (**II**) in $PhNO_2$–N_2. C_5H_5N–C_6H_5N,HCl or AcOH hydrolyses (**IV**) to 9 : 10-dibenzoylphenanthrene (**VI**), so that condensation of (**VI**) with NH_2Ph is impossible. Dissolution of (**IV**) in C_5H_5N and addition of aq. N_2H_4 gives the azine, m.p. 335—336°, of (**VI**). H_2O_2 converts (**IV**) in warm AcOH or HCO_2H into (**VI**). H_2S converts (**IV**) in boiling C_5H_5N into (**V**). With MgPhBr in Et_2O–PhMe and then aq. NH_4Cl, (**IV**) gives 9-*benzoyl*-10-α-*hydroxybenzhydrylphenanthreneanil*, m.p. 279—280° (decomp.) [azenium *perchlorate*, m.p. 342 (decomp.), and *picrate* m.p. 233—234° (decomp.)]. PhNO and (**I**) in boiling C_5H_5N–N_2 give 1 : 2 CO_2–CO and a mixture including 1 : 2 : 3 : 4 : 5-*pentaphenylpyrrole*, m.p. 282° (no salts), also obtained (m.p. 283°) from (**I**) and boiling $PhNO_2$ or tetraphenylfuran (**VII**), NH_2Ph,HCl, and Al_2O_3 at 400°. (**VII**) does not react with *p*-$NH_2{\cdot}C_6H_4{\cdot}NMe_2$,HCl. R. S. C.

Attempts to find new antimalarials. XVIII. D. C. Quin and (Sir) R. Robinson. **XIX.** W. L. Glen and (Sir) R. Robinson. **XX.** (Miss) J. Crum and (Sir) R. Robinson (*J.C.S.*, 1943, 555—556, 557—561, 561—565).—XVIII. Condensation of 8-amino-6-methoxyquinoline (**I**) with *o*-$C_6H_4(CO)_2N{\cdot}[CH_2]_2{\cdot}Br$ gives 8-β-*phthalimidoethyl*-6-*methoxyquinoline*, m.p. 153—155°. $OPh{\cdot}[CH_2]_3{\cdot}NH_2$ and *o*-$C_6H_4(CO)_2N{\cdot}[CH_2]_3{\cdot}Br$ in dioxan afford *phthalo*-γ-(γ′-*phenoxypropylamino*)*propylimide hydrobromide*, m.p. 184°, which with HBr yields the *phthalo*-γ-(γ′-*bromo*)-compound, m.p. 195°. This salt with (**I**) gives 8-γ-*phthalimidopropyl*-γ-*aminopropylamino*-6-*methoxyquinoline dihydrobromide*, m.p. 222—223°, which with N_2H_4 yields 8-γ-*aminopropyl*-γ-*aminopropylamino*-6-*methoxyquinoline trihydrochloride*, almost devoid of antimalarial activity; the latter was thought to be the most probable structure for R.63 (cf. Robinson, *et al.*, A., 1934, 1368). 1 : 2 : 4-$C_6H_3Cl(NO_2)_2$ and $(CH_2{\cdot}NH_2)_2$ in EtOH afford 2 : 4-*dinitro*-β-*aminoethylaniline*, m.p. 54° [*hydrochloride*, m.p. 250° (decomp.)], which with $OPh{\cdot}[CH_2]_3{\cdot}Br$ and K_2CO_3 in EtOAc forms 2 : 4-*dinitro*-N-γ-*phenoxypropyl*-β-*aminoethylaniline hydrochloride*, m.p. 114°. 8-γ-Phthalimidopropylamino-6-methoxyquinoline (**II**) and *o*-$C_6H_4(CO)_2N{\cdot}[CH_2]_3{\cdot}Br$ give a mixture, from which is separated, as the hydrobromide, 8-*di*-γ-*phthalimidopropylamino*-6-*methoxyquinoline*, m.p. 166°, which with N_2H_4 yields 8-*bis*-γ-*aminopropylamino*-6-*methoxyquinoline trihydrochloride*, a weak antimalarial. 5-Chloro-8-amino-6-methoxyquinoline, m.p. 154° (lit. 150—152°), with $Cl{\cdot}[CH_2]_2{\cdot}NEt_2$,HCl affords ο-*chloro*-8-β-*diethylaminoethylamino*-6-*methoxyquioline*, m.p. 76°, which has weak antimalarial properties. 2 : 5-Dichloro-7-methoxyacridine with 8-γ-aminopropylamino-6-methoxyquinoline (**III**) and PhOH gives 2-*chloro*-ο-(6′-*methoxyquinolyl*-8′-γ-*aminopropylamino*)-7-*methoxyacridine*, m.p. 114° [*dihydrochloride*, m.p. 223° (decomp.)], and with (**II**), 2-*chloro*-5-γ-*phthalimidopropylamino*-(N-6′-*methoxy*-8′-*quinolyl*)-7-*methoxyacridine*, m.p. 253° (decomp.), is obtained.

XIX. New preps. of R.63 have been made, and the high antimalarial activity is confirmed. Fractionation of the *dimeconate* (+$2H_2O$), decomp. ~150—160° (corresponding *tartrate*), has afforded no specimen of higher activity and in some cases a reduction of activity has occurred in all fractions without traceable loss of material. No light has been shed on the nature of R.63 by the synthesis of various substances that might have been produced in the formation reaction. (**III**) forms a *dimeconate* (+H_2O), m.p. 165—166° (decomp.). $Br{\cdot}[CH_2]_{10}{\cdot}Br$, *o*-$C_6H_4(CO)_2NH$, and K_2CO_3 give *phthalo*-ω-*bromodecylimide* (**IV**), m.p. 57—58°, which with (**I**) affords 8-ω-*phthalimidodecylamino*-6-*methoxyquinoline*, m.p. 83—84° [*hydrochloride*, m.p. 151—153° (decomp.)], converted by N_2H_4 into the 8-ω-*NH*$_2$-compound, isolated as the *dihydrochloride*, m.p. 172° (R.95). This base with (**IV**) yields 8-ω-*aminodecyl*-ω-*aminodecylamino*-6-*methoxyquinoline*, isolated as the *meconate* (weak antimalarial). (**III**) and (**IV**) heated together, followed by treatment with N_2H_4, give 8-ω-*aminodecyl*-γ-*aminopropylamino*-6-*methoxyquinoline*, isolated as the *meconate*, m.p. 160—164°. (**III**) with $Cl{\cdot}[CH_2]_{11}{\cdot}NEt_2$,HCl gives a substance(meconate, R.97, m.p. ~155°, a potent antimalarial), the salts of which could not be cryst. $CHEtCl{\cdot}[CH_2]_2{\cdot}NEt_2$,HCl and (**III**) condense to a substance (meconate, R.113, decomp. 160—165°, a potent, non-toxic, antimalarial), whilst a similar substance [meconate, R.103, m.p. 150—155° (decomp.)] is obtained from (**III**) and $CHMeBr{\cdot}[CH_2]_3{\cdot}NEt_2$,HBr. *p*-$NHAc{\cdot}C_6H_4{\cdot}SO_2Cl$ and (**III**) afford 8-γ-p-*acetamidobenzenesulphonamidopropylamino*-6-*methoxyquinoline*, m.p. 189°.

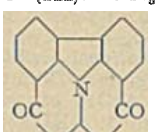
$NEt_2\cdot[CH_2]_{11}\cdot Cl,HCl$ with 5-chloro-8-amino-6-methoxyquinoline gives *5-chloro-8-ω-diethylaminoundecylamino-6-methoxyquinoline hydrochloride*, m.p. 126—128°. $Br\cdot[CH_2]_{10}\cdot CO_2Et$ and (I) lead to *8-ω-carbethoxydecylamino-6-methoxyquinoline*, m.p. 43—47°, successively converted into the *acid*, m.p. 110—111°, and *amide*, m.p. 113—114°. $Br\cdot[CH_2]_{11}\cdot CN$ and (I) give *8-ω-cyanodecylamino-6-methoxyquinoline*, m.p. 84—85°, which is converted through the imino-ether hydrochloride with EtOH–NH_3 into the *8-ω-guanyl* derivative, isolated as the *hydrochloride* ($+H_2O$), m.p. 76—77°. A similar prep. from 8-aminoquinoline affords *8-ω-cyano-*, m.p. 60—61°, and *-guanyl-decylaminoquinoline*, isolated as the *hydrochloride*, m.p. 92—93°. The appropriate reagents yield *8-γ-cyano-*, m.p. 52—53°, and *-guanyl-propylaminoquinoline* (*hydrochloride*, m.p. 152—154°). 6-Acetamidoquinaldine and $o\text{-}C_6H_4(CO)_2N\cdot[CH_2]_3\cdot Br$ give *ψ-6-acetamido-2-methyl-1-γ-phthalimidopropylquinolinium bromide*, m.p. 240—245° (decomp.), which with $p\text{-}NMe_2\cdot C_6H_4\cdot CHO$ affords *ψ-6-acetamido-2-p-dimethylaminostyryl-1-γ-phthalimidopropylquinolinium bromide*, converted by HBr into *ψ-6-amino-2-p-dimethylaminostyryl-1-γ-aminopropylquinolinium bromide hydrobromide* (no antimalarial properties, but is antiseptic and trypanocidal).

XX. A method for including *sec.*-amine end groups in the basic side-chain in antimalarials of the plasmoquin series has been devised by alkylation of (I) by means of a chlorohydrin, replacement of OH in the product by Cl, and interaction of the chloroalkylamino-compound with primary bases. The general formula of the bases is (V) and in the substances described $x = 3$. Interesting variations of antimalarial activity of the compounds are recorded. Trimethylenechlorohydrin, (I), and $C_8H_{17}\cdot OH$ give *8-γ-hydroxy-propylamino-6-methoxyquinoline*, m.p. 53°, which with $SOCl_2$ affords the *-Cl*-compound (VI), b.p. 115°/0·0001 mm., and some *bis-(8-γ-chloropropylamino-6-methoxy-5-quinolyl) sulphide*, m.p. 144° [*hydrochloride* ($+3H_2O$), m.p. 200—201°]. The latter compound with $NHEt_2$ forms the *bis-8-γ-NEt$_2$-* derivative (R.118), m.p. 85° [*hydrochloride* ($+H_2O$), m.p. 150° (decomp.)]. Condensation of (VI) with the appropriate amine affords *8-γ-methyl-* (R.105), b.p. 166°/0·5 mm. (*H oxalate*, m.p. 188°; *hydrochloride*, m.p. 218°), *-ethyl-* (R.106) [*H oxalate*, m.p. 139°; *hydrochloride* ($+H_2O$), m.p. 206°], *-propyl-* (R.119) (*hydrochloride*, m.p. 162°; *H oxalate*, m.p. 173°), *-isopropyl-* (R.108) (*H oxalate*, m.p. 136°; *hydrochloride*, m.p. 210°), *-n-butyl-* (R.107) [*H oxalate* ($+H_2O$), m.p. 141°; *picrate*, m.p. 178°; *hydrochloride* ($+H_2O$), m.p. 180°], *-isobutyl-* (R.110) [*H oxalate* ($+H_2O$), m.p. 218°; *hydrochloride*, m.p. 178°], *-tert.-butyl-* (R.109) (*meconate*, m.p. 188°; *hydrochloride*, m.p. 174°), *-n-heptyl-* (R.114) (*H oxalate*, m.p. 181°; *hydrochloride*, m.p. 110—112°), *-benzyl-* (R.117) [*H oxalate*, m.p. 230°; *hydrochloride* ($+0·5H_2O$), m.p. 204°], *-cyclohexyl-* (*H oxalate*, m.p. 215°), *-furfuryl-* (R.112) [*H oxalate* ($+H_2O$), m.p. 209°; *hydrochloride* ($+EtOH$), m.p. 203°], *-diethyl-* (rhodoquin, R.116) (*dimeconate*, m.p. 178°; *hydrochloride*, m.p. 208°), and *-methylpropyl-aminopropylamino-6-methoxyquinoline* (R.123) [*meconate* ($+H_2O$), m.p. 168°; *picrate*, m.p. 152—154° (decomp.); *hydrochloride* ($+1·5H_2O$), m.p. 180—184°]; and *8-β′-phenylisopropyl-* (R.111) [*H oxalate* ($+H_2O$), m.p. 128°; *hydrochloride*, m.p. 127°], *-β′-aminoethyl-* (R.115) [*H oxalate*, m.p. 221°; *meconate* ($+3H_2O$), m.p. 186° (decomp.); *hydrochloride*, m.p. 244°], *-γ′-aminopropyl-* (R.120) [*H oxalate*; *hydrochloride* ($+0·5H_2O$), m.p. 225° (decomp.)], *-δ′-amino-n-butyl-* (R.121) [*H oxalate* ($+H_2O$), m.p. 183—185°; *hydrochloride* ($+H_2O$), m.p. 210°], *-ε-amino-n-amyl-* (R.122) (*H oxalate*, m.p. 162°; *hydrochloride*, m.p. 196°), *-β-hydroxyethyl-* [*picrate*, m.p. 159° (decomp.); *hydrochloride*, m.p. 98°, remelts 154°], and *-β-hydroxyethylmethyl-γ-aminopropylamino-6-methoxyquinoline* [*meconate* ($+H_2O$), m.p. 128° (decomp.); *hydrochloride*, m.p. 212°]. R.120 is devoid of antimalarial properties, and it is now certain that R.63 owes its activity to some other constituent. F. R. S.


(V.)

Oxidations with selenium dioxide. W. Borsche and H. Hartmann (*Ber.*, 1940, **73**, [*B*], 839—842; cf. A., 1938, II, 202).—2-Methylpyridine is oxidised by SeO_2 in boiling EtOAc to small amounts of pyridine-2-aldehyde (phenylhydrazone, m.p. 178—179°; 2 : 4-*dinitrophenylhydrazone*, m.p. 239—240°) and some pyridine-2-carboxylic acid. Under similar conditions 1 : 2 : 3 : 4-tetrahydroacridine is partly oxidised to 4-keto-1 : 2 : 3 : 4-tetrahydroacridine [*dinitrophenylhydrazone*, m.p. 273—274° (decomp.), and its *hydrochloride*, decomp. 255°] but mainly dehydrogenated to acridine. Similarly the 2-Me derivative is in part oxidised to 4-keto-2-methyl-1 : 2 : 3 : 4-tetrahydroacridine (*dinitrophenylhydrazone*, decomp. 257—258°) but mainly dehydrogenated. On the other hand in so far as it reacts 7-aza-5 : 6-benzhydrindene is converted into the -hydrindone (*dinitrophenylhydrazone*, darkens and decomp. >300°). Dimethyldihydroresorcinol and SeO_2 in boiling EtOAc give anhydrodimethone selenium oxide, $\begin{matrix}CH_2\text{—}CO\cdot C\cdot ScO\cdot C\cdot CO\text{—}CH_2\\ \|\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\|\\ CMe_2\cdot CH_2\cdot C\text{—}O\text{—}C\cdot CH_2\cdot CMe_2\end{matrix}$ [*bisdinitrophenylhydrazone*, m.p. 281—282° (cf. Stamm *et al.*, A., 1933, 1314)]. Under similar conditions $\beta\text{-}C_{10}H_7\cdot OH$ affords *dihydroxydinaphthyl selenide*, m.p. 195—196°, which gives a dark green colour with $FeCl_3$, dissolves unchanged in NaOH, couples with PhN_2Cl, and yields a *dibenzoate*, m.p. 213—214°. H. W.

Relative reactivities of organo-metallic compounds. LIII. Dimetallation of 9-phenylcarbazole. H. Gilman and C. G. Stuckwisch (*J. Amer. Chem. Soc.*, 1943, **65**, 1729—1733).—9-Phenylcarbazole (I) (0·082) with $LiBu^a$ (0·25 mol.) in Et_2O and then CO_2 gives 9-phenylcarbazole-2′-carboxylic (II) and -2′ : 6′-*dicarboxylic acid* (III) (25%), m.p. 273—274° [by decarboxylation gives 87% of (II) (cf. A., 1942, II, 122)]. CH_2N_2 gives the Me_2 ester, m.p. 156—157°, of (III). PCl_5 and then $SnCl_4$ in xylene at 0° converts (III) into *benz*[i]*carbazolo*[1 : 9 : 8-cdef]*quinolizine*-7 : 11-*dione* (IV), m.p. 228—230°, which gives a *mono-oxime*, m.p. 262—264°, but does not condense with *l*-menthyl *N*-aminocarbamate. Carbazole-1-carboxylic acid, m.p. 275—276°, is obtained from Mg 9-carbazolyl bromide and CO_2 at >1 atm. in 18% yield; its Me ester, m.p. 98—100°, with $o\text{-}C_6H_4I\cdot CO_2Me$, K_2CO_3, and Cu-bronze in boiling $PhNO_2$ and then 30% KOH gives *9-phenylcarbazole-1 : 2′-dicarboxylic acid*, m.p. 231—232° (*Me*$_2$ ester, m.p. 144—145°), cyclised as above into (IV) (proof of structure). Similar condensations gives *9-phenylcarbazole-2 : 2′-*, m.p. 266—267° (*Me*$_2$ ester, m.p. 146—147°), *-3 : 2′-*, m.p. 246—247° (*Me*$_2$ ester, m.p. 143—144°), and *-2′ : 4′-dicarboxylic acid*, m.p. 278—280° (*Me*$_2$ ester, m.p. 160—161°). 1 : 3 : 2-$C_6H_3Me_2I$ (V) and boiling aq. $KMnO_4$ give 2 : 1 : 3-$C_6H_3I(CO_2H)_2$, m.p. 260° (decomp.) (lit. 205—220°, 236°). Condensation of 2 : 1 : 3-$C_6H_3I(CO_2Me)_2$ and carbazole (VI) and then hydrolysis gives only 70% of $[C_6H_3(CO_2H)_2\text{-}2 : 6]_2$, m.p. 390° (decomp.). No products are obtained by condensing (VI) with (V). The Li_2 derivative of (I) with Me_2SO_4 in Et_2O gives an inseparable mixture. Conc. HNO_3 converts (III) in AcOH at 100° into the 3 : 6-$(NO_2)_2$-derivative, m.p. >350°, which by decarboxylation gives 3 : 6-*dinitro-9-phenylcarbazole*, m.p. 298°, obtained from 3 : 6-dinitrocarbazole by PhI; HNO_3 in AcOH at room temp. gives *3-nitro-9-phenylcarbazole-2′ : 6′-dicarboxylic acid*, m.p. 282—284°, which by decarboxylation gives 3-nitro-9-phenylcarbazole and resists cyclisation. R. S. C.


(IV.)

Hydrolysis of substituted barbituric acids under pressure. H. Ruhkopf (*Ber.*, 1940, **73**, [*B*], 938—940).—H_2O at 5 atm. hydrolyses substituted barbituric acids to 1 : 1 mixtures of acyl-ureides and -amides ($+CO_2 + NH_3$), but at 10 atm. the amide is the sole product. At 5 atm. salts of strong acids favour formation of ureide, those of weak acids lead to mainly ureide, and alkalis cause further hydrolysis to the acid. *E.g.*, 5 : 5-diethylbarbituric acid in H_2O at 5 atm. gives $CHEt_2\cdot CO\cdot NH\cdot CO\cdot NH_2$ (I) (47%) and $CHEt_2\cdot CO\cdot NH_2$ (II) (~40%), but in aq. NaCl at 3 atm. gives 80% of (I). 5 : 5-Diallylbarbituric acid in H_2O at 10 atm. gives 95% of $(CH_2{:}CH\cdot CH_2)_2CH\cdot CO\cdot NH_2$. In aq. Na_2SO_3 at 5 atm. 5-phenyl-5-ethylbarbituric acid gives 80% of $CHPhEt\cdot CO\cdot NH_2$. 1-Methyl-5 : 5-diethylbarbituric acid in H_2O at 10 atm. gives (II), CO_2, and NH_2Me. R. S. C.

Heterocyclic nitrogen compounds. Stereochemistry of tervalent nitrogen. H. H. Hatt and (Miss) E. F. H. Stevenson (*J. Amer. Chem. Soc.*, 1943, **65**, 1785—1786).—Known compounds having the ring-system of 1 : 2-trimethylenepyrazolidine (Buhle *et al.*, A., 1943, II, 207) are listed. R. S. C.

Pyrazole compounds. IV. Acylation of 3-phenyl- and 3-anilino-5-pyrazolone. A. Weissberger and H. D. Porter (*J. Amer. Chem. Soc.*, 1943, **65**, 1495—1502; cf. A., 1943, II, 280).—3-Phenyl-5-pyrazolone with Ac_2O or Ac_2O–AcOH at 100° gives 62—66% of the 1-Ac derivative (II), m.p. 127—128° (lit. 121°), and >20% of *5-acetoxy-3-phenylpyrazole* (III), m.p. 150—152° (cf. Curtius, A., 1895, i, 246; von Rothenburg, *ibid.*, 686). NaOH hydrolyses (II) and, more readily, (III) to (I). (II), but not (III), is sol. in Na_2CO_3. (II) gives a magenta dye with $p\text{-}NO\cdot C_6H_4\cdot NMe_2$ (IV) or in the film-strip test with $p\text{-}NH_2\cdot C_6H_4\cdot NMe_2$ (Fischer, *Phot. Korr.*, 1914, **51**, 19). (II) and (III) are equilibrated in boiling 66% AcOH, but C_5H_5N converts (II) irreversibly into (III); thus (III) is best prepared by treating (I) in C_5H_5N with Ac_2O at 100° or AcCl at room temp. Further treatment of (I), (II), or (III) with Ac_2O or of (III) with AcCl–C_5H_5N gives *1-acetyl-5-acetoxy-3-phenylpyrazole* (V), m.p. 84° [previously (*loc. cit.*) considered to be the 1 : 2-diacetoxypyrazolone], insol. in Na_2CO_3 but slowly hydrolysed to (I) by NaOH, to (II) by boiling piperidine–EtOH, and to (III) by hot 66% AcOH. Ac_2O and (I) give also a small amount of *1-acetyl-3-acetoxy-5-phenylpyrazole* [? 1 : 2-*diacetyl-3-phenyl-5-pyrazolone*], m.p. 75—76°, insol. in Na_2CO_3, which is also obtained from (V) by Ac_2O–AcOH, is hydrolysed by NaOH to (I) and by 66% AcOH to (III), and with hot piperidine–EtOH gives *3-hydroxy-1-acetyl-5-phenylpyrazole*, m.p. 144—146°, sol. in Na_2CO_3, hydrolysed to (I) by NaOH, and giving no dye by either test. With BzCl–C_5H_5N at 100°, (I) gives *5-benzoyloxy-3-phenylpyrazole* (VI), m.p. 170—171°, insol. in NaOH, reconverted into (I) by piperidine–EtOH and with Ac_2O at 100° or with AcCl–C_5H_5N giving *1-acetyl-5-benzoyloxy-3-phenylpyrazole*, m.p. 108—109°, which is hydrolysed to (I) by piperidine–EtOH. With BzCl in C_5H_5N, (VI) gives *1-benzoyl-5-benzoyloxy-3-phenylpyrazole* (VII), m.p. 117—118°, but in PhMe some *1-benzoyl-3-benzoyloxy-5-phenylpyrazole* (VIII), m.p. 181—182°, is also obtained; the structures assigned to (VII) and (VIII) may perhaps be reversed. (VII) and (VIII) are insol. in aq. NaOH but with NaOH–EtOH give (I);

treatment with piperidine gives erratic results; HCl in dioxan gives (VI) from (VII) or (VIII). With Ac_2O at 100° (5 min.) or Ac_2O (1 mol.)–C_5H_5N, 3-anilino-5-pyrazolone (IX) gives *3-anilino-1-acetyl-5-pyrazolone* (X), m.p. 207—209° (decomp.), sol. in Na_2CO_3, hydrolysed to (IX) by NaOH, and giving with (IV) a magenta dye containing Ac and formed also in the film-strip test. With Ac_2O at 100° (30 min.), (IX) or (X) gives *3-anilino-1-acetyl-5-acetoxypyrazole* (XI), m.p. 131°, insol. in Na_2CO_3 [converted by piperidine (1 mol.) or aq. AcOH into (IX)], and a small amount of *5-anilino-1-acetyl-3-acetoxypyrazole* (XII), m.p. 108—109°, insol. in Na_2CO_3, hydrolysed by NaOH to (IX) and by piperidine to *3-hydroxy-5-anilino-1-acetylpyrazole*, m.p. 203—205° (decomp.), sol. in Na_2CO_3, giving (IX) by NaOH, but yielding negative dye tests. Boiling AcOH causes transformation of (XI) into (XII), but (X) is unaffected. (XII) is best obtained by boiling (IX) in Ac_2O. When heated with Bz_2O or BzCl (2 mols.) + H_2O (1 mol.) in C_5H_5N, (IX) gives *3-anilino-5-benzoyloxypyrazole*, m.p. 148—150°, insol. in Na_2CO_3 and hydrolysed to (IX) by piperidine; heating with BzCl–C_5H_5N in absence of H_2O gives *3-anilino-1-benzoyl-5-pyrazolone*, m.p. 198—200° (decomp.), relatively stable to NaOH, sol. in Na_2CO_3, and giving positive dye tests; BzCl in dioxan at 100° yields *3-anilino-1-benzoyl-5-benzoyloxypyrazole*, m.p. 132—134°, insol. in Na_2CO_3. R. S. C.

Synthesis of purine nucleosides. III. 4-Glycosidaminopyrimidines. IV. 4 : 6-Diaminopyrimidine. New synthesis of pyrimidine derivatives. G. W. Kenner, B. Lythgoe, A. R. Todd, and A. Topham (*J.C.S.*, 1943, 571—574, 574—575).—III. Direct glycosidisation of 4-aminopyrimidines is complicated since such compounds may behave as derivatives of 4-iminodihydropyrimidine. *d*-Xylose, 4 : 6-diamino-2-methylthiopyrimidine (I), and NH_4Cl in EtOH give *6-amino-4-d-xylosidamino-2-methylthiopyrimidine* (II), m.p. 190—192° (decomp.), hydrolysed to (I), isolated as the *picrate*, m.p. 212° (decomp.). Ac_2O, AcCl, and (II) in C_5H_5N afford *6-acetamido-4-triacetyl-d-xylosidamino-2-methylthiopyrimidine*, m.p. 226°, $[\alpha]_D^{18}$ +5·1° in C_5H_5N, which with MeOH–NaOMe yields the *6-acetamido*-4-d-compound, m.p. 95—100°, or 192—193° (hydrated), $[\alpha]_D^{20}$ +23° in C_5H_5N. Acetylation with EtOAc–AcCl of (I) affords the *hydrochloride* (+H_2O), m.p. 213—214°, of the Ac derivative. *6-Amino-4-d-mannosidamino-2-methylthiopyrimidine* (+1·5H_2O), m.p. 213—214° (decomp.), similarly prepared, gives rise to *6-acetamido-4-tetra-acetyl-d-* (+3H_2O), m.p. 140—150°, $[\alpha]_D^{20}$ −100° in C_5H_5N, and *-4-d-mannisidamino-2-methylthiopyrimidine*, m.p. 242—243° (decomp.), $[\alpha]_D^{0}$ −55° in C_5H_5N. 4 : 6-Diamino-2-methylpyrimidine, *d*-xylose, EtOH, and HCl give *6-amino-4-d-xylosidamino-2-methylpyrimidine*, m.p. 219° (decomp.), $[\alpha]_D$ +158° in H_2O (constitution proved by hydrolysis).

IV. 4 : 6-*Dichloropyrimidine*, m.p. 67·5°, prepared from the corresponding $(OH)_2$-compound and $POCl_3$–$NPhMe_2$, under pressure at 170° with NH_3–EtOH gives some 4 : 6-$(NH_2)_2$-compound (III). Small yields of (III) are also obtained from 4 : 6-diamino-2-thiolpyrimidine with NaOAc and H_2O_2, and from 6-iodo-4-aminopyrimidine with NH_3–EtOH at 180—200°. *Malondi-iminoether dihydrochloride*, obtained from $CH_2(CN)_2$ and HCl–EtOH, with cold NH_3–EtOH affords *malondiamidine dihydrochloride*, which with Na–MeOH, followed by HCO_2Et, gives (III). F. R. S.

Pyrimidines.—See B., 1944, II, 7.

Synthesis and properties of ninhydrin ureide. D. D. Van Slyke and P. B. Hamilton (*J. Biol. Chem.*, 1943, **150**, 471—476).—Ninhydrin (I) (1 mol.) and $CO(NH_2)_2$ (II) (1 mol.) combine in boiling 0·1N-H_2SO_4 to form *ninhydrin "ureide"* (III), $C_{10}H_{10}O_5N_2$, or after loss of 7·6% H_2O in vac. at 56°, $C_{10}H_8O_4N_2$, m.p. 216—217° (decomp.); there may be anhydride formation or H_2O of crystallisation. In boiling H_2O, at pH 2, (III) undergoes partial degradation or hydrolysis, with loss of CO_2 and possible decomp. to (I) + (II). (I) has a retarding effect (noted after 1 min.) on evolution of CO_2 from (II) at 100°. From the velocity of the combination of (I) and (II), conditions are defined which enable (II) to be removed from solution nearly quantitatively by formation of (III). A. T. P.

Formation and properties of azlactones obtained from vanillin substitution products. L. C. Raiford and C. H. Buurman (*J. Org. Chem.*, 1943, **8**, 466—472).—The following *2-phenyl-4-3'-methoxy-4'-acetoxybenzylideneoxazol-5-ones* (azlactones) are obtained by heating the requisite substituted vanillin (I) with hippuric acid (II) and NaOAc in Ac_2O at 100°: *5'-chloro-*, m.p. 190·5—191·5°; *6'-chloro-*, m.p. 205—206°; *5' : 6'-dichloro-*, m.p. 239—240°; *5'-bromo-*, m.p. 191—191·5°; *6'-bromo-*, m.p. 211°; *5' : 6'-dibromo-*, m.p. 265°; *2' : 5' : 6'-tribromo-*, m.p. 190·5—191°; *5'-bromo-4'-methyl-*, m.p. 167·5—168·5°; *5'-iodo-*, m.p. 180—181°. 2-Bromohippuric acid, m.p. 193—194°, similarly affords *2-2'-bromophenyl-4-3'-methoxy-4'-acetoxybenzylideneoxazol-5-one*, m.p. 158·5—159·5°, and its *5'-*, m.p. 187—188°, and *6'-Br-*, m.p. 197—198°, *5 : 6-Br_2-*, m.p. 225—226°, and *2 : 5 : 6-Br_3-*, m.p. 189—191°, -derivatives. Aceturic acid yields the following *4-3' : 4-dimethoxybenzylidene-2-methylpyrazol-5-ones* by condensation with the appropriate vanillin derivative: *5'-chloro-*, m.p. 203—204°; *5'-chloro-4'-methyl-*, m.p. 169—170°; *5'-bromo-*, m.p. 206—207°; *5'-bromo-4'-methyl-*, m.p. 162—163°; *6'-bromo-*, m.p. 119—120°; *5'-iodo-*, m.p. 196—197°. Cautious heating of the azlactone (III) from (I) and (II) with ~3% KOH gives α-benzamidoferulic (α-benzamido-4-hydroxy-3-methoxycinnamic) acid, m.p. 208·5—209·5°, reconverted into (III) by Ac_2O at 100°. The following substituted *4-hydroxy-3-methoxycinnamic acids* are obtained analogously: *5-chloro-α-acetamido-*, m.p. 212—213°; *4-chloro-α-benzamido-*, m.p. 227—228°; *5-bromo-α-acetamido-*, m.p. 203—204°; *5-bromo-α-benzamido-*, m.p. 229—230°; *5-iodo-α-acetamido-*, m.p. 217—218°; *5-iodo-α-benzamido-*, m.p. 227—228°. *α-Acetamido-* and *5-bromo-α-benzamido-3 : 4-dimethoxycinnamic acids* have m.p. 198—199° and 201—202° respectively. *Et*, m.p. 196—197°, and *Me*, m.p. 205—206°, *5-bromo-α-benzamido-4-hydroxy-3-methoxycinnamate* and *Me 5-bromo-α-benzamido-3 : 4-dimethoxycinnamate*, m.p. 119—121°, have been prepared. The azlactones are converted by boiling 6N-NaOH into NH_3, BzOH, and the following *4-hydroxy-3-methoxyphenylpyruvic acids*: *5-chloro-*, m.p. 228—228·5° (*oxime*, m.p. 158—159°); *5-bromo-*, m.p. 237·5—239°/(decomp.) [*oxime*, m.p. 169° (decomp.); *semicarbazone*, m.p. 195—196°; *diacetate*, m.p. 193—194°]; *5-iodo-*, m.p. 234—235° (*oxime*, m.p. 170—171°). *5-Bromo-3 : 4-dimethoxyphenylpyruvic acid*, m.p. 175—177°, gives a *Me ether*, m.p. 162—163°. H. W.

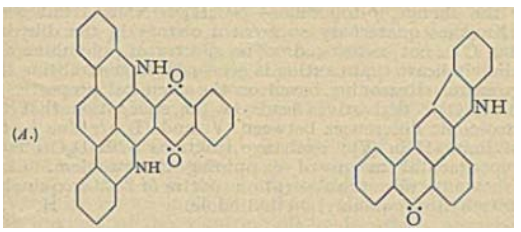
Hydroindazolone derivatives; search for new analgesics. C. W. Picard and D. E. Seymour (*Quart. J. Pharm.*, 1943, **16**, 264—269; cf. A., 1944, III, Mar.).—A simplified method for prep. of 1-phenyltetrahydroindazolone (I) consists in condensing Et *cyclo*hexanone-2-carboxylate (II) with a salt of $NHPh{\cdot}NH_2$ instead of the free base; similarly condensation of (II) with N_2H_4,H_2SO_4 in H_2O yields tetrahydroindazolone. Condensation of (I) with the appropriate alkyl halide in boiling EtOH–KOH yields *1-phenyl-2-n-*, m.p. 65·5°, and *-iso-propyl-*, m.p. 84—85°, *-2-n-butyl-*, an oil, m.p. 84°, and *-iso-amyl*, an oil, and *-2-allyl-tetrahydroindazoline*, m.p. 65—67°. (I) with BzCl in C_5H_5N gives the *2-Bz* derivative, m.p. 110°. Treatment of 1-phenyl-2-methyltetrahydroindazolone with $ClSO_3H$ and subsequently with NH_3 yields *2-p-sulphonamidophenyl-1-methyltetrahydroindazolone*, m.p. 272—273°. *1-p-Acetamidobenzenesulphonyl-2-phenyltetrahydroindazolone* has m.p. 190—191°. J. N. A.

Further diacridines and diacridylium salts. K. Gleu and R. Schaarschmidt (*Ber.*, 1940, **73**, [*B*], 909—915).—Acridones (I) are reduced to "diacridines" by methods which must be adapted to the individual cases (Zn and HCl–EtOH are frequently useful) and these are readily oxidised to diacridylium nitrates by boiling dil. HNO_3. Alternatively (I) are treated with Mg+MgI_2 in boiling PhOMe; the resulting pinacols are too unstable for isolation and, after removal of the solvent with steam, the diacridylium salts are usually immediately obtained as the sparingly sol. iodides, which are readily converted into the nitrates and chlorides. The following are described: 10 : 10'-*diethyl" diacridine,"* m.p. 275°; 10 : 10'-*diethyldiacridylium H nitrate*, $C_{30}H_{26}N_2(NO_3)_2,HNO_3,3H_2O$; 10 : 10'-*diphenyl" diacridine,"* m.p. 342°; 10 : 10'-*diphenyldiacridylium nitrate* and *chloride*, $C_{38}H_{26}N_2Cl_2,2HCl,8H_2O$, and the *compound*, $C_{38}H_{26}N_2Cl_2,ZnCl_2,H_2O$; 10 : 10'-*dimethyldiacridylium nitrate tetra-* and *di-hydrate*. 10 : 10'-Diethyl- and -dimethyl-acridylium salts show green luminescence of about the same intensity. The chemiluminescence colour of the 10 : 10'-Ph_2 compounds in very dil. solution is pure blue comparable in shade and intensity with that of 3-aminophthalhydrazide; the fluorescence colour is pure green so that in this instance there is a distinct difference between fluorescence and chemiluminescence. Further, the chemiluminescence colour depends on the concn. whereas the fluorescence colour is not materially affected. The concn. of H_2O_2 is also significant. It appears therefore that the chemiluminescence phenomenon is more complex than assumed hitherto and that there is no general identity between fluorescence- and chemiluminescence-spectra; the identity sometimes observed is accidental. Diacridines show marked chemiluminescence in org. media in which autoxidation occurs without addition of alkali; it is best observed by addition of EtOH to a diacridine in *cyclo*hexanone. H. W.

Pyridazine derivative of cholestanedione.—See A., 1944, II, 52.

***ms*-Benzacridan derivatives.** H. Waldmann and K. G. Hindenburg [with S. Back] (*J. pr. Chem.*, 1940, [ii], **156**, 157—168).—1-Anilino-2 : 3-benzanthraquinone is converted by $AlCl_3$ (10 parts) at 150° (bath)/2 hr. or by 75% H_2SO_4 (20 parts) at 180°/8 hr. into 2 : 3-*benzcæramidonine*, m.p. 262°. 1-Amino-2 : 3-benzanthraquinone, *o*-$C_6H_4Cl{\cdot}NO_2$, K_2CO_3, $Cu(OAc)_2$, and Cu powder in boiling $PhNO_2$ give the *1-o-nitroanilino-*, m.p. 283° [less readily obtained from 1-chloro-2 : 3-benzanthraquinone (I), *o*-$NO_2{\cdot}C_6H_4{\cdot}NH_2$, K_2CO_3, and $Cu(OAc)_2$ in $PhNO_2$], reduced (EtOH–Na_2S) to the *1-o-amino-anilino*-derivative, m.p. 264°, which with $NaNO_2$ in aq. AcOH at −6° to 0° affords *1-1'-benztriazolyl-2 : 3-benzanthraquinone*, m.p. 288° [also prepared from (I), benztriazole (II), KOAc, and $Cu(OAc)_2$ in $PhNO_2$]; this in boiling $NHPh_2$ gives 3 : 4-*phthaloyl-ms-benzacridan*, m.p. 289—290°. *1-o-Chloroanilino-2 : 3-benzanthraquinone*, m.p. 206°, is obtained from (I), *o*-$C_6H_4Cl{\cdot}NH_2$, and NaOAc. 1 : 4-Dichloro-2 : 3-benzanthraquinone (III), (II), KOAc, and $Cu(OAc)_2$ in $PhNO_2$ at 190° (bath) give *1 : 4-di-1'-benztriazolyl-2 : 3-benzanthraquinone*, decomp. 291° (also formed by HNO_2 on the 1 : 4-di-*o*-aminoanilino-derivative), which in boiling $NHPh_2$ affords 1 : 2-

phthaloyl-4 : 5 : 8 : 9-*dibenzo*-3 : 10-*dihydro*-3 : 10-*diazapyrene* (*A*), m.p. >400° (obtained directly if the original reaction mixture is boiled). 4-Chloro-1-hydroxy-2 : 3-benzanthraquinone, (II), KOAc, and $Cu(OAc)_2$ in $PhNO_2$ at 220—230° give 2-*hydroxy*-3 : 4-*phthaloyl*-ms-*benzacridan*, m.p. >310°. *ang*.-Naphthotriazole with (I) and (III) in boiling $PhNO_2$ similarly affords the *mono*-, m.p. 319° (decomp.), and *di*-*naphthotriazolyl* derivatives, m.p. >340°, respectively, and thence 3 : 4-*phthaloyl*-5 : 6(7 : 8)-*benzo*-ms-*benzacridan*, m.p. 290° (in boiling $NHPh_2$), and 1 : 2-*phthaloyl*-4 : 5 : 8 : 9-*di*-1′ : 2′(2′ : 1′)-*naphtho*-3 : 10-*dihydro*-3 : 10-*diazapyrene*, m.p. >400°. 3 : 4-*Phthaloyl*-6 : 7-*benzo*-ms-*benzacridan*, m.p. >320°, and 1 : 2-*phthaloyl*-4 : 5 : 8 : 9-*di*-2′ : 3′-*naphtho*-3 : 10-*dihydro*-3 : 10-*diazapyrene*, m.p. >400°, are similarly obtained directly using *lin*.-naphthotriazole. *lin*.-Naphthotriazole-4 : 9-quinone with (I) and (III) in boiling $PhNO_2$ similarly affords the *mono*-, m.p. >370°, and *di*-*naphthotriazolequinonyl* derivative, m.p. >400°, respectively, from which N_2 could not be eliminated. 3-Bromobenzanthrone (IV), *o*-$NO_2{\cdot}C_6H_4{\cdot}NH_2$, KOAc, and $Cu(OAc)_2$ in boiling $PhNO_2$ give the 3-*o*-*nitroanilino*-, m.p. 266°, reduced (EtOH–Na_2S) to the 3-*o*-*aminoanilino*-derivative, m.p. 268°. This with $NaNO_2$ in aq. AcOH at >−2° affords 3-1′-*benztriazolylbenzanthrone*, m.p. 306·5° [less readily obtained from (II) and (IV)], which in boiling anthracene gives the *carbazole* derivative (*B*), m.p. 348° [cautious oxidation (CrO_3, AcOH) gives anthraquinone-1-carboxylic acid]. H. B.



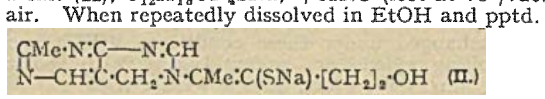
Isolation of mononucleotides after hydrolysis of ribonucleic acid by crystalline ribonuclease. H. S. Loring and F. H. Carpenter (*J. Biol. Chem.*, 1943, **150**, 381—388).—The NH_4 salt of ribonucleic acid (I) (yeast-nucleic acid is used) in neutral or slightly acid medium is treated with cryst. ribonucleinase (preferable to the term ribonuclease; cf. Kunitz, A., 1941, III, 47) at room temp. at pH 6·3 (decreases to 5·5). Four acids are obtained: guanylic [purified through the dibrucine salt, $+7H_2O$, sinters at 210°, decomp. 224° (immersed at 200°), and Na_3 salt, $[\alpha]_D^{23}$ −57·6° in aq. NaOH], uridylic [dibrucine salt, $+7H_2O$, $[\alpha]_D^{28}$ −54·4° in C_5H_5N; $(NH_4)_2$ salt, shrinks at 170—175°, decomp. 183° (immersed at 165°), $[\alpha]_D$ +20·0° in H_2O], cytidylic, decomp. 230°, and adenylic, $+H_2O$, decomp. 196°, $[\alpha]_D^{24}$ −38° in H_2O. These four nucleotides are not formed during fractionation processes, as they could not be obtained in experiments in which nucleic acid, in absence of enzyme, is fractionated. A. T. P.

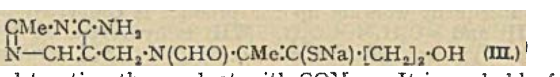
New method for isolation of crystalline adenine nucleotides. M. V. Buell (*J. Biol. Chem.*, 1943, **150**, 389—394).—The following reaction is characteristic of adenine mononucleotides and of yeast-nucleic acid (I): addition of solutions containing picrate + Al ions (at pH 2·4) [*e.g.*, $Al(OAc)_3$ + picric acid] affords (mainly) an Al picrate complex of the nucleotide. The method is used for the isolation of cryst. adenine nucleotide (II). Thus, the K acetate salt of guanine nucleotide is pptd. by 95% EtOH from a neutral solution of (I), previously treated with 0·3-N aq. KOH for 24 hr. at room temp. The filtrate then affords the Al picrate salt of (II); after dissolution in morpholine and pptn. with $COMe_2$, the salt is converted by aq. KOH + AcOH (pH 5) into (II), $+2H_2O$ (purified through the Pb salt). Cryst. adenylic acid (III) is isolated from beef heart. Enzyme action is inhibited by freezing the muscle, and proteins are removed from an aq. extract by heat-coagulation and picric acid pptn. (III) is obtained from the filtrate as the Hg salt, then pptd. as the Al picrate complex, and purified through the Pb salt. A. T. P.

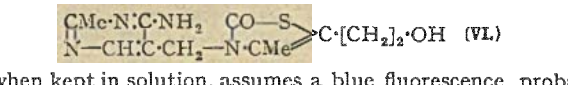
Fluorescent irradiation products of thiazole. R. Stampfli (*Helv. Physiol. Pharm Acta*, 1943, **1**, C54—55).—"Vitachrome" is most strongly fluorescent (deep blue) in acid solution. It is heat-stable, lowers surface tension, and is stable to long-wave ultra-violet radiation. Fluorescent substances were obtained from 2-thiol-4 : 5-dimethylthiazole, 2-thiol-4-methyl-5-acetoxyethylthiazole, Na 2-thiol-4-methylthiazolecarboxylate, and 2-thiol-4-methylthiazole; the last two prioducts show max. fluorescence at alkaline pH. Negative results were obtained with 4-methylthiazole and its nitrate, 2-amino-4-methylthiazolium nitrate, 3-benzyl-4-methyl-5-β-hydroxyethylthiazolium chloride, 3 : 4-dimethyl-5-hydroxymethylthiazolium chloride, 4-methyl-3-acetoxyethylthiazolium bromide, 4-methyl-3-diethylaminoethyl-5-hydroxyethylthiazolium chloride, 4-methylbenzylthiazolium chloride. A. S.

Conversion of 2-phenyl-4-chloromethylthiazole into 5-chloro-2-phenyl-4-hydroxymethylthiazole. E. H. Huntress and K. Pfister, tert. (*J. Amer. Chem. Soc.*, 1943, **65**, 1667—1670).—2-Phenyl-4-chloromethylthiazole (I) [obtained from $CO(CH_2Cl)_2$ and $PhCS{\cdot}NH_2$ with subsequent hydrolysis by conc. HCl; 71% yield], m.p. 48·2—51·2°, with boiling 0·1N-NaOH or KOAc–AcOH gives 2-*phenyl*-4-*hydroxy*- (II), m.p. 66—69°, and 2-*phenyl*-4-*acetoxymethylthiazole*, m.p. 42—43° [also obtained from (II)], respectively. CrO_3–H_2SO_4–H_2O oxidises (II) to 2-*phenylthiazole*-4-*carboxylic acid* (22%), m.p. 175—176·5° [*acid chloride* (III), m.p. 97·7—98·5°; *amide*, m.p. 143·3—143·8°]. With NaI–$COMe_2$, (I) gives 2-*phenyl*-4-*iodomethyl*-, m.p. 103·5—104·6°, and with NaCN–EtOH gives 2-phenyl-4-cyanomethyl-thiazole, m.p. 43·1—44·2°, b.p. 147—148°/2 mm. (lit. 180—185°/4—5 mm.), hydrolysed by boiling 6N-HCl to 2-phenyl-4-thiazolylacetic acid, m.p. 88·8—89·8° (lit. 90°) [Na salt; hydrochloride, m.p. 203·1—205·1° (gas) (lit. 206—207°)]. Boiling conc. HNO_3–H_2O (10 : 24 ml.) converts (I) into 5-*chloro*-2-*phenyl*-4-*hydroxymethylthiazole* (57·5%), m.p. 116·5—118° (*acetate*, m.p. 63·3—64·1°; 3 : 5-*dinitrobenzoate*, m.p. 155·1—155·3°), which with CrO_3–H_2SO_4–H_2O gives 5-*chloro*-2-*phenylthiazole*-4-*carboxylic acid* (41·6%), m.p. 198·8—199·3° (gas), also obtained in 21% yield with 2-phenylthiazole-4-carboxylic acid (54%) from (III) by HNO_3–H_2O. 29·2% of BzOH is obtained from (II) by dil. alkaline $KMnO_4$. M.p. are corr. (block). R. S. C.

Oxidation product of aneurin effective antineuritically. O. Zima and R. R. Williams (*Ber.*, 1940, **73**, [*B*], 941—949).—Triturating aneurin chloride hydrochloride (I) with saturated, aq. K_2CO_3 at room temp. gives the quaternary *chloride*, $C_{12}H_{17}ON_4ClS$, decomp. when heated. In NaOEt–EtOH, (I) gives a yellow colour and yields a yellow *Na* salt (II), $C_{12}H_{15}ON_4SNa$, $+3H_2O$ (lost at 78°/vac.), unstable in air. When repeatedly dissolved in EtOH and pptd. therefrom by Et_2O, this gives a colourless *Na* salt (III), $+4H_2O$, converted over $CaCl_2$ at room temp./vac. into a *dihydrate*, but becoming yellow at 110°. (III) is also obtained by adding aq. NaOH to (I) in H_2O at 0° and treating the product with $COMe_2$. It is probably formed by way of the quaternary hydroxide. (II) and (III) do not give a nitroprusside reaction, but the reaction is not characteristic in this series as it fails also with (I) and five related thiazole derivatives. The yellow colour in alkali is fairly characteristic of (I) but is no criterion of antineuritic activity as it is given also by the 4-Me isomeride. When (III) is treated in H_2O at 0° with aq. I–KI, 1 I is rapidly absorbed and thereafter more is absorbed very slowly; use of 1 I leads to the colourless *disulphide* (IV), $+Bu^{\alpha}OH$, m.p. 173°, or $+COMe_2 + H_2O$, obtained anhyd. (m.p. 177°) by EtOH–Et_2O (*dihydrochloride*, m.p. 231°). (IV) becomes yellow when melted and dissociates in high-boiling solvents, but its mol. wt. is correctly given in MeOH by Menzies and Wright's method (A., 1921, ii, 622). Benzthiazole methiodide and I give a similar disulphide, which does not dissociate. Zn–HCl reduces (IV) to (I); boiling HCl–EtOH–H_2O hydrolyses it to 6-amino-2-methyl-5-aminomethylpyrimidine, but boiling NaOEt regenerates (I). In boiling $(CH_2{\cdot}OH)_2$, (IV) gives thiochrome (V) and a *product* (VI), $C_{12}H_{16}O_2N_4S$, m.p. 233—234°, which, when kept in solution, assumes a blue fluorescence, probably by formation of (V). (VI) has <60—70% of the antineuritic effect (rats) of (I). (I) may be the reduced form of the natural "redox" system. R. S. C.







Cyanine dyes etc.—See B., 1944, II, 7, 10.

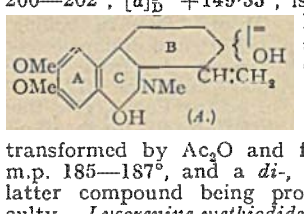
VII.—ALKALOIDS.

Constitution of yohimbine and its degradation products. B. Witkop (*Annalen*, 1943, **554**, 83—126).—It is shown that the OH group of yohimbine (I) is attached to $C_{(17)}$. (I) has m.p. 234°, new $[\alpha]_D^0$ +62·2° in EtOH; technical samples of its hydrochloride may contains a little *iso*yohimbine but the presence of *allo*yohimbine is excluded. Decarboxylation of yohimboaic acid (II) by NaOH–CaO cannot be effected at <350° and gives the ketone *yohimbone* (III), m.p. 307° (decomp.) [*methiodide*, m.p. ~290° (decomp.), darkens at 250°; *methochloride* ($+2H_2O$), m.p. 276° (decomp.); *hydrochloride* of 2 : 4-*dinitrophenylhydrazone*, m.p. >300°, darkens at 280°]. Rapid treatment of (II) with TlOH at 300°/0·1 mm. gives *deoxy*-*yohimbol*, m.p. 149°, $[\alpha]_D^{20}$ −24·8° in C_5H_5N (*hydrochloride*, m.p. 228°; *picrate*, m.p. 224°; *methiodide*, m.p. 198°; the *methochloride* is physiologically inactive in the frog). The mother-liquors from (III) contain indole and *iso*quinoline derivatives so that direct crystallisation is impossible but treatment with MeI in MeOH leads to the isolation of *yohimbol methiodide*, m.p. 282° (decomp.) (corresponding *methochloride*, m.p. 259°, softens at 245°). At 260° (II) evolves CO_2 but gives a non-crystallisable residue. In presence of Cu powder decarboxylation occurs at 225°, giving (III) in 8% yield; mol. Ag and Ag_2O are without influence. (III) is obtained in good yield from

(II) mixed with anthracene at 320°, and in poor yield from (II) and aq. $Ba(OH)_2$ at 280°. Slow decarboxylation of (II) with NaOH–CaO at 270—300° leads to "tetrahydroyobyrine" (IV), m.p. 166°. Dehydrogenation of (I) by $Al(OPh)_3$ and *cyclo*hexanone in xylene at 150° gives (III), $[\alpha]_D^{20}$ −105·8° in C_5H_5N (*hydrochloride*, m.p. 328°; *picrate*, m.p. 171°), similarly obtained from (II); attempts to isolate the intermediate "yohimbinone" under milder conditions were unsuccessful. (III) is dehydrogenated by black Se at 300° to tetrahydroyobyrine, m.p. 167° (hydrochloride, m.p. 236°), and yobyrine, m.p. 215° [picrate, m.p. 239° (much decomp.)], but does not appear to be affected by $Pb(OAc)_4$. *allo*Yohimboaic acid and $Al(OPh)_3$ in boiling *cyclo*hexanone–xylene afford *allo*yohimbone, m.p. 230° (decomp.) (2 : 4-*dinitrophenylhydrazone*, darkens at 250° and softens and swells at 264°), whilst under similar conditions yohimbenic acid affords *yohimbenone*, m.p. 268° (decomp.) (2 : 4-dinitrophenylhydrazone hydrochloride darkens at 260°, softens at 280°). (III), $Al(OPr^{\beta})_3$, and $Pr^{\beta}OH$ in xylene afford *yohimbol* (V), m.p. 243° (decomp.), $[\alpha]_D^{20}$ −63·4° in EtOH, −55·4° in MeOH [*hydrochloride* (+0·5H_2O), m.p. 291°, $[\alpha]_D^{20}$ −51·5° in MeOH], and epi*yohimbol* (VI), $C_{19}H_{24}ON_2$, m.p. 258°, $[\alpha]_D^{20}$ −80·1° in MeOH (*methiodide*, m.p. >300° after darkening and softening; *methochloride*, m.p. 298°); a short period of reaction favours (V) whilst with very protracted action the yield of (VI) is >50%. (IV) (*hydrochloride*, m.p 236°) is dehydrogenated by Pd sponge at 280° to 2:3-*isoquinolyl*-3-*ethylindole*, m.p. 128° (*hydrochloride*, m.p. 212°; *methiodide*, m.p. 192°), isomeric with yobyrine (VII) [*hydrochloride*, m.p. 271° (much decomp.), softens at 240°; *picrate*, m.p. 239° (decomp.)], which remains unchanged under these conditions. (VII) is oxidised by SeO_2 in boiling xylene or, preferably, Ac_2O to *yobyrone* (VIII), $C_{19}H_{14}ON_2$, m.p. 185°, which does not react with $(NO_2)_2C_6H_3{\cdot}NH{\cdot}NH_2$ in dil. HCl. (VII) is converted by paracetaldehyde at 260° into *ethylideneyobyrine*, m.p. 298° (darkening); with p-$NO_2{\cdot}C_6H_4{\cdot}CHO$ a similar condensation occurs at 180—200° but in subsequent working up the product is converted by acid into (VIII) and o-$C_6H_4Me{\cdot}CO_2H$. (VII) is hydrogenated (PtO_2 in AcOH at 40°) to *hexahydroyobyrine*, m.p. 197°. *apo*Yohimbine (IX) is oxidised by $Pb(OAc)_4$ in AcOH at 40° and then hydrolysed to *tetrahydroyobyrinecarboxylic acid* (X), m.p. 286° (decomp.), $[\alpha]_D^{20}$ +217·6° in EtOH [*hydrochloride* (+2H_2O), m.p. 303° (much decomp.), $[\alpha]_D^{20}$ +307·3° in EtOH], oxidised by SeO_2 in boiling C_5H_5N to tetrahydroyobyronecarboxylic acid [*hydrochloride semihydrate*, m.p. 244° (decomp.)], which does not react with 2 : 4-$(NO_2)_2C_6H_3{\cdot}NH{\cdot}NH_2$ in dil. HCl. *Hydroxyhexahydroyobyrinecarboxylic acid* ["*tetradehydroyohimboaic acid*"] (+H_2O), m.p. 325°, is not obtained in the same manner as (X) but is best prepared through the ester hydrochloride; the presence in it of active CH_2 is proved by the reduction of SeO_2 in C_5H_5N. *Yohimboaic acid sulphate hydrochloride*, m.p. 308° (decomp.) [free *sulphate*, m.p. 289° (decomp.)], is converted by HCl in boiling MeOH followed by NH_3 into ε-*yohimbine*, m.p. 203° (darkening), softens at 195°, $[\alpha]_D^{20}$ +29·8° in C_5H_5N, and (I). Boiling KOH–MeOH hydrolyses (IX) to *apoyohimboaic acid*, m.p. 306° (decomp.), with two *bases*, $C_{21}H_{24}O_2N_2$, m.p. 201° (decomp.), becomes yellow at 160°, and $C_{21}H_{24(26)}O_{2(3)}N_2$, m.p. 228°. In 50% of AcOH containing Pd–C under H_2 (IX) passes into α-iso*yohimbine*, m.p. 304°, $[\alpha]_D^{20}$ +53·2° in 50% AcOH, hydrolysed to α-iso*yohimboaic acid* (+1·5H_2O), m.p. 238°, and converted by NaOAc and boiling Ac_2O into (IX); oxidation (Oppenauer) of it does not give a base or CO-acid. The isolation of p-cresol by the distillation of (I) with Zn dust is described. The physiological activity of many quaternary bases of the yohimbine series is discussed. For these experiments the methiodides are frequently too sparingly sol. and must be converted into the methochlorides. apo*Yohimbine methiodide monohydrate*, effervesces at 259° after softening at 246° and becoming brown at 220°, appears new. H. W.

Constitution of derivatives of the harman series from the viewpoint of their ultra-violet spectra. F. Pruckner and B. Witkop (*Annalen*, 1943, **554**, 127—144).—Comparison of the absorption spectra of norharman (I) and yobyrine (II) leads to the conclusion that substitution in (I) at $C_{(3)}$ causes a marked diminution in the intensity in band II to an extent which exceeds the enhancement caused by addition of the extinction of the xylene residue. The spectrum of (I) and still more that of (II) is very similar to that of carbazole. The diminished height of the bands with (II) may be due to substitution as such which diminishes the symmetry of the mol. This effect is yet more prominent in the comparison of the spectra of (II) and tetrahydroyobyrinecarboxylic acid; the extinction vals. of hydroxyhexahydroyobyrinecarboxylic acid (which has nearly the same position of the bands) could not be measured. Similar results are recorded for papaverine (III)–*iso*quinoline (IV) in which substitution causes a displacement of all bands towards the red and exaltation of the extinction is caused by the addition of an aromatic ring separated by a CH_2 group; this is particularly noticeable in band II. The complete absence from the spectrum of (III) of the individual bands seen in that of (IV) is ascribed to the presence of OMe in (III). In support of this hypothesis it is observed that the individual bands of indole are absent from the spectra of 5- and 6-methoxyindole; similar observations are recorded for lepidine and p-methoxylepidine. The spectrum of harmine (V) differs considerably from that of harmaline (VI), which behaves optically more like a derivative of indole than a hydrogenated harman. Further evidence in the same direction is based on the observation that the spectrum of (VI) does not differ so greatly from that of its methiodide as do the spectra of the methiodides of (V) and (II) differ from those of the *tert.*-bases. This difference shows that (V) and (II) are closely related in spite of the differences in their spectra. The transition of (V) into the quaternary salt causes a weakening of the aromatic system similar to that caused by the change, p-toluidine → p-$C_6H_4Me{\cdot}NMe_3Cl$ but when N of (VI) becomes quaternary so great a change in the dihydropyridine ring C is not occasioned. The spectra of yohimbine and its methiodide indicate that caution is necessary in generalising this line of argument. Reasoning based on the chemical properties of indole and its OMe derivatives leads to the conception that the great spectroscopic differences between (V) and (I) are due to the mobility of imino-H in (V); exchange reactions with D_2O offer a possible experimental means of examining the problem. Close analogy is shown between the absorption spectra of 2 : 2′-*iso*quinolyl- and 2 : 2′-tetrahydro*iso*quinolyl-3-ethylindole. H. W.

Lycoris **alkaloids. XVI. Constitution of lycorenine.** H. Kondo and T. Ikeda (*Ber.*, 1940, **73**, [*B*], 867—874).—Lycorenine (I), m.p. 200—202°, $[\alpha]_D^{23}$ +149·33°, is *A*. Catalytic hydrogenation (Pd or PtO_2 in AcOH) of (I) gives *dihydrolycorenine*, m.p. 175—177°, or under more drastic conditions *deoxytetrahydrolycorenine*, m.p. 165—168°, with *compounds*, $C_{18}H_{\sim 23(25)}O_3N$, m.p. 120—123°, and $C_{18}H_{27}O_2N$, m.p. 165—167°. (I) is transformed by Ac_2O and fused NaOAc at 100° into a mono-, m.p. 185—187°, and a *di*-, m.p. 173—176°, -*acetyl-lycorenine*, the latter compound being produced with much the greater difficulty. *Lycorenine methiodide*, decomp. 260°, is converted by AgOH followed by distillation at 130°/vac. mainly into the amorphous α-methine base (analysed as the *methiodide*, $C_{18}H_{20}O_3NMe_2I$, decomp. 223°), with a smaller proportion of amorphous β-methine base. de-N-*Lycorenine* (II), m.p. 114·5°, is $C_{15}H_{10}O(OMe)_2$. One O is lost as H_2O in the first stage of the degradation and the residual O is present in CO and not in OH since (II) cannot be acetylated but affords an *oxime*, $C_{17}H_{16}O_2{\cdot}N{\cdot}OH$, m.p. 147—150°. The B nucleus is readily aromatised during the Hofmann degradation by the formation of a new double linking owing to loss of H_2O, and :CH·OH at $C_{(8)}$ passes into CHO whilst N is eliminated. Ozonisation of (II) leads to CH_2O, a *dialdehyde* (III), $C_{16}H_{14}O_4$, m.p. 155—157° (*disemicarbazone*, decomp. 238°), and an aldehydic *acid*, $C_{16}H_{14}O_5$, m.p. 228—230° (p-*nitrophenylhydrazone*, decomp. 276—278°), also obtained by oxidising (III) with $KMnO_4$ in $COMe_2$ at room temp., and further oxidised to a dicarboxylic *acid*, $C_{16}H_{14}O_6$, m.p. 256—257° (Me_2 ester, m.p. 135—137°). This is characterised as 3 : 4-*dimethoxydiphenyl*-6 : 3′-*dicarboxylic acid* by hydrolysis of the Me ester obtained synthetically from 3 : 4 : 6 : 1-$(OMe)_2C_6H_2Br{\cdot}CO_2Me$, m-$C_6H_4I{\cdot}CO_2Me$, and Cu powder at 255—260°. CH_2O is readily obtained by the action of O_3 on (I) but the aldehydic base formed simultaneously is too unstable for further examination. Like a typical ψ-base (I) affords an *oxime hydrochloride*, decomp. 258°. H. W.



Strychnos **alkaloids. XCII. Reactions of *N*-methyl*sec.*-ψ-brucine and related bases.** H. Leuchs and H. G. Boit (*Ber.*, 1940, **73**, [*B*], 885—892).—An amended method of obtaining ψ-brucine (I) is reported. The action of MeI on (I) in MeOH gives 7% of quaternary salt against 3—4% in H_2O but the quaternary salt observed previously (A., 1939, II, 349) is not encountered when (I), free from brucine, is produced. With ψ-brucine Me ether and MeI the yields of *tert.* base and quaternary salt are 39 and 61% in presence of MeOH and 60 and 40% in presence of H_2O. Reaction of (I) with Me_2SO_4 yields exclusively *tert.*-*N*-Me base. Dihydro-ψ-brucine Me ether and MeI in H_2O afford *N*-methyldihydro-ψ-brucine methiodide in 84% yield; this forms ~25% of the product from dihydro-ψ-brucine. Methylation of (I) may be expected to occur in accordance with the scheme, :C(OH)·N: → :CO·NMe· but the product does not react with $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$ or with NH_2OH,HCl in C_5H_5N and $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$ does not affect the quaternary methiodide or its H_2-derivative. MnO_4' oxidises (I) at 20° in $COMe_2$ but with 10 equivs. of O_2 ~40% remains unchanged and the rest is altered in an ill-defined manner. The Me base is converted by MnO_2 and SO_2 into two isomeric *sulphonic acids*, $C_{24}H_{27}O_5N_2{\cdot}SO_3H$, $[\alpha]_D^{20}$ −120·3°/*d* and 41°/*d* in 2 mols. of 0·1N-NaOH; the homogeneity of a third material, $[\alpha]_D^{20}$ −62·3°/*d*, is not established. With PhCHO in boiling NaOMe–MeOH it yields *benzylidene*- (II), m.p. 234—236° (vac.), reduced (Na–Hg in dil. MeOH containing a little AcOH) to *benzyl-N-methyl*sec.-ψ-*brucine*, m.p. 195—197° (vac.) (*hydrobromide*; *perchlorate*). Hydrogenation (PtO_2 in 25% AcOH) of (II) leads to *benzyldihydro*-N-*methyl*sec.-ψ-*brucine* [*hydrobromide* (+H_2O), m.p. 105—110° to a resin or, anhyd., m.p. 215—225° (slight decomp.); *hydrochloride*, m.p. ~100° and 215—225°]. (I) condenses with PhCHO to benzylidene-ψ-brucine, isolated as the *hydrobromide*, chars at 225°, reduced by Na–Hg in dil. MeOH to a mixture of benzyl-

ψ-brucine and -brucine hydrobromide and hydrogenated (PtO_2 in 50% AcOH) to benzyldihydro-ψ-brucine (*hydrochloride*, m.p. ~220° after softening; darkens at 190°). The *tert.* ether base obtained by the action of NaOMe or Na–Hg on *N*-methyl-ψ-brucine methiodide is hydrolysed by 12N-HCl at 100° to *N*-methyl*sec.*-ψ-brucine. The methiodide of this base is reduced by Na–Hg–H_2O to the methiodide, $C_{26}H_{36}O_5N_2$,MeI, m.p. 276—278°; other methods of treatment lead to a neutral *perchlorate*, $(C_{26}H_{34}O_5N_2)_2,HClO_4$, m.p. 102°, decomp. 112°, and a *base*, $C_{25}H_{32}O_5N_2$, m.p. 230—233° (vac.), which contains only 2 OMe and hence has suffered an Emde fission. This base absorbs 4 H when hydrogenated (PtO_2 in 0·1N-HCl) and according to conditions gives two interconvertible *salts*, $C_{25}H_{36}O_5N_2,HClO_4$, hydrated, m.p. 114—115° (decomp.), softens at 100°, anhyd. m.p. 263—269°, and $C_{25}H_{36}O_5N_2,2HClO_4$, m.p. 153—154° (decomp.); the corresponding bases are non-cryst. but another experiment gives a cryst. *base*, $C_{25}H_{34(36)}O_5N_2$, m.p. 172° in <10% yield. H. W.

Veratrine alkaloids. XIV. Correlation of the veratrine alkaloids with the solanum alkaloids. L. C. Craig and W. A. Jacobs (*Science*, 1943, **97**, 112).—5-Methyl-2-ethylpyridine (**I**) was isolated from the distillate from solanidine and Se. (**I**) is a characteristic degradation product of the veratrine alkaloids, which are probably C_{27} compounds closely related to the sterols. E. R. R.

VIII.—ORGANO-METALLIC COMPOUNDS.

Chemistry of bivalent and tervalent rhodium. V. Co-ordination complexes of rhodous halides with dialkylarsines.—See A., 1944, I, 46.

Synthetic application of *o*-β-bromoethylbenzyl bromide. II. Preparation and properties of 2-substituted 1 : 2 : 3 : 4-tetrahydro-*iso*arsinolines. III. Preparation and optical resolution of 2-phenyl-2-*p*-chlorophenacyl-1 : 2 : 3 : 4-tetrahydro*iso*arsinolinium bromide. F. G. Holliman and F. G. Mann (*J.C.S.*, 1943, 547—550, 550—554).—II. *o*-Br·$[CH_2]_2$·C_6H_4·CH_2Br (**I**) in Et_2O with $AsPhCl_2$ and Na–EtOAc in absence of air give 2-*phenyl*-1 : 2 : 3 : 4-*tetrahydro*iso*arsinoline* (**II**), b.p. 110—112°/0·01 mm. (*methiodide*, m.p. 136—137°), which is oxidised by HNO_3 to the oxy-compound, isolated as the *hydroxy-nitrate*, m.p. 149—150°; by Br–$CHCl_3$ to the arsine dibromide, isolated as the iso*arsinoline dichloride*, m.p. 147—149°, or as 2-*phenyl*-1 : 2 : 3 : 4-*tetrahydro*iso*arsinoline sulphide*, m.p. 124° (by H_2S), and by chloramine-*T* to the oxy-compound, isolated as the *hydroxy-picrate*, m.p. 116—118°. $AsMeCl_2$ with (**I**) in a similar manner affords 2-*methyl*-1 : 2 : 3 : 4-*tetrahydro*iso*arsinoline* (**III**), b.p. 131°/18 mm. (*methiodide*, m.p. 179—181°; *methopicrate*, m.p. 163—164°), which is oxidised with HNO_3 to the hydroxy-nitrate, isolated as the *hydroxy-picrate*, m.p. 164—165·5°. Cl_2 in CCl_4 converts (**III**) into 2-*methyl*-1 : 2 : 3 : 4-*terahydro*iso*arsinoline dichloride*, which at 130—140° gives MeCl and 2-*chloro*-1 : 2 : 3 : 4-*tetrahydro*iso*arsinoline*, b.p. 157°/14 mm., unaffected by boiling C_5H_5N. 2-*Phenyl*-1 : 2 : 3 : 4-*tetrahydro*iso*phosphinoline*, b.p. 130—160°/0·2 mm. (*methiodide*, m.p. 116—118°), can be prepared in small yield only. None of the compounds tested possesses trypanocidal or antimalarial activity.

III. *p*-C_6H_4Cl·CO·CH_2Br and (**II**) give dl-2-*phenyl*-2-p-*chlorophenacyl*-1 : 2 : 3 : 4-*tetrahydro*iso*arsinolinium bromide*, m.p. 190—191° (dl-*iodide*, m.p. 190·5°), which with Ag *d*-bromocamphorsulphonate yields the d-*bromocamphorsulphonate*, m.p. 119—131°, $[M]_D^{16}$ +279°. Crystallisation from C_6H_6–*cyclo*hexane affords the l-iso*arsinolinium* d-*bromocamphorsulphonate*, m.p. 236—238°, $[M]_D^{16}$ −140°, which is converted into the *picrate*, $[M]_D^{16}$ −450°, and *iodide*, m.p. 178·5—179°, $[M]_D^{19}$ −352°. The Ag *l*-salt similarly gives d-iso*arsinolinium* l-*bromocamphorsulphonate*, m.p. 236—237°, α_D^{16} +0·89°, from which the *picrate*, $[M]_D$ +457° is obtained. 2-*Phenyl*-2-p-*chlorophenacyl*-1 : 2 : 3 : 4-*tetrahydro*iso*arsinolinium* d-*camphorsulphonate*, m.p. 210—212°, $[M]_D^{16}$ +112°, similarly prepared, gives the *chloroplatinate*, m.p. 211—213°, and *chloroaurate*, 157—158°. The picrates and iodide are optically stable in $CHCl_3$ at room temp. These are the first arsonium salts to be obtained in optically stable forms, and the correlation of their optical and chemical stability provides strong evidence that the optical instability previously recorded for dissymmetric arsonium salts has been due to the formation of a " dissociation-equilibrium " in solution. The properties of other dissymmetric 4-covalent As compounds are discussed on this basis. All rotations are in $CHCl_3$. F. R. S.

Autoxidation of lead tri*cyclo*hexyl and its behaviour towards carbon tetrachloride. F. Hein, E. Nebe, and W. Reimann (*Z. anorg. Chem.*, 1943, **251**, 125—160).—PbR_3 (R = *cyclo*hexyl) in solution is stable towards O_2 in the dark but undergoes oxidation in light thus: $4PbR_3 + 5O_2 = PbR_2O + 2PbO + PbO_2$ + other products. The only intermediate product is $(PbR_3)_2O$. PbR_3 reacts with CCl_4 in presence of O_2 in the dark at room temp., giving PbR_3Cl, PbR_2Cl_2, $PbRCl_3$, CO_2, and Cl_2, and even in absence of O_2 affords PbR_3Cl, PbR_2Cl_2, and C_2Cl_6. Free CCl_3 is an intermediate product. CBr_4 and C_2Br_6 react similarly but even more energetically. Mechanisms are suggested. F. J. G.

Introduction of water-solubilising groups into some organometallic compounds. R. W. Leeper (*Iowa State Coll. J. Sci.*, 1943, **18**, 57—59).—The following were prepared: *$PbPh_3$ H maleate*, m.p. 207°, *$(PbPh_3)_2$ maleate*, sinters 198—199°, *Pb triphenyl* o-*hydroxyphenyl*, m.p. 216—218°, *$PbPh_3$ 9-phenanthryl*, m.p. 169—171°, *$PbPh_2$ di-9-phenanthryl*, m.p. 208—210°, *$PbPh_3$* 7-(1 : 2-*benzanthryl*), m.p. 295—296°, *PbPh* di*cyclohexyl chloride*, m.p. 195°, decomp. 205°, *$PbPh_2$ Et chloride*, sinters 142°, decomp. 146—147°, *$Pb(C_6H_4·NO_2$-m$)_2$ dichloride*, sublimes 250°, decomp. 285—289° (*di-iodide*, decomp. 135°), *$GeBu^a_3$ iodide*, b.p. 126—128°/4 mm., *Ge tetra*-2-*furyl*, b.p. 163°/1 mm., m.p. 99—100°, *$SnBu^a$ tri-iodide*, b.p. 154°/5 mm., *Sn di-carbethoxymethyl dibromide*, m.p. 139°. F. R. G.

Organolead compounds containing water-solubilising groups. D. S. Melstrom (*Iowa State Coll. J. Sci.*, 1943, **18**, 65—67).—RHal with $LiBu^a$ in Et_2O gives LiR which with CO_2 yields RCO_2H, the following being new: 2 : 4 : 5-*triphenylfuran*-3-, m.p. 257—258° (*Me* ester, m.p. 123·5—124°), 3 : 4 : 6-*triphenylpyridine*-2-*carboxylic acid*, m.p. 166—168° (decomp.) (*Me* ester, m.p. 117—118°) p-*carboxyphenylethyl alcohol*, m.p. 127—128°, α-p-*carboxyphenylethyl alcohol*, m.p. 138—139°. The reaction of LiR with $PbPh_2Cl$ leads to the formation of *$PbPh_3$* o- (**I**), m.p. 134—136°, m-, m.p. 113—114°, and p-*hydroxymethylphenyl* (**II**), m.p. 98—100°; *$PbPh_3$* p-β-, m.p. 87—88°, and -α-*hydroxyethylphenyl*, m.p. 68—70°. (**II**) was oxidised ($KMnO_4$) to *$PbPh_3$* p-*carboxyphenyl*, m.p. 256—258° (*Me* ester, m.p. 125—127°; *Na* and *K* salts). Similarly (**I**) produces the *anhydride* of *$PbPh_2$* o-*carboxyphenyl hydroxide*, m.p. 300—305° (with turbidity) [*chloride*, m.p. 210—220° (with turbidity) (*Me* ester, m.p. m.p. 170—171°)]. Also prepared were p-*phenylenedi*(*lead triphenyl*), m.p. 285—288° and *$PbPh_3$* o-*anisyl*, m.p. 128—129°. F. R. G.

Long-chained organometallic compounds. R. N. Meals (*Iowa State Coll. J. Sci.*, 1943, **18**, 62—64).—The following were prepared: *Hg di*-n-*dodecyl*, m.p. 44—44·5°, *-tetradecyl*, m.p. 53—54°, *-hexadecyl*, m.p. 61—62°, and *-octadecyl*, m.p. 66·5—67°; *Hg* n-*dodecyl*, m.p. 114—114·5°, *-hexadecyl*, m.p. 114—115°, and *-octadecyl chloride*, m.p. 115—116°; *Hg* n-*dodecyl*, m.p. 108—108·7°, *-tetradecyl*, m.p. 110—110·5°, *-hexadecyl*, m.p. 110·5—111·5°, and *-octadecyl bromide*, m.p. 110—111°; *Hg* n-*dodecyl*-, m.p. 91°, and *-hexadecyl iodide*, m.p. 93; *Sn tetra*-n-*dodecyl*, m.p. 15—16°, *-tetradecyl*, m.p. 33—34°, *-hexadecyl*, m.p. 41·5—42·5°, and *-octadecyl*, m.p. 47°; *Pb tetra*-n-*tetradecyl*, m.p. 31°, and *-hexadecyl*, m.p. 42°; *Sn tri*-n-*dodecyl*, m.p. 33°, *-tetradecyl*, m.p. 46—47°, *-hexadecyl*, m.p. 55·5—56·5°, and *-octadecyl chloride*, m.p. 61—62°; *Pb tri*-n-*dodecyl*, m.p. 64—65°, *-tetradecyl*, m.p. 74—75°, *-hexadecyl*, m.p. 79—80°, and *-octadecyl chloride*, m.p. 82—83°; *tri-dodecyl*-, b.p. 200°/0·009 mm., and *-tetradecyl-arsine*. F. R. G.

Organotin compounds. C. E. Arntzen (*Iowa State Coll. J. Sci.*, 1943, **18**, 6—9).—A survey. The following were prepared (Grignard): *$SnPh_3$* o-, m.p. 176—177° (decomp.), and p-*hydroxy*-, m.p. 201—203°, *$SnPh_2$* o-*hydroxy*-, m.p. 136—138°, *$SnPh_3$* o-, m.p. 158—159°, and p-*hydroxymethyl*- (**I**), m.p. 98—100°; *$SnPh_2$* o-*methoxymethyl*-, m.p. 94·5—95·5°; *$SnPh_3$* o-, m.p. 110—112°, and p-*dimethylamino-phenyl* (**II**), m.p. 132—134°. (**I**) is oxidised ($KMnO_4$) to *$SnPh_3$* p-*carboxyphenyl*, m.p. 166—168°. Coupling of (**II**) yields *$SnPh_3$* 4-*dimethylamino*-3-(4′-*nitrobenzeneazo*)*phenyl*, m.p. 190—192°. F. R. G.

Organothallium compounds. R. K. Abbott, jun. (*Iowa State Coll. J. Sci.*, 1943, **18**, 3—5).—Sol., non-toxic compounds were prepared from $TlAryl_2$ and AgX (X = solubilising acid group); *$TlPh_2$ sulphanilate*, m.p. 345° (decomp.), *Tl Me_2*, m.p. 231—233°, *Et_2* m.p. 220—221°, and *Ph*, *saccharate*, m.p. 315—320° (slight decomp.), *Tl di*-2-*pyridyl lactate*, m.p. 205—208° (decomp.). With fuming H_2SO_4 at −20° *Tl(o-$C_6H_4Me)_2Br$* yields *Tl di*-2-(4-*sulphotolyl*) *sulphate* (*Na* salt). Nitration of *$TlPh_2$·NO_3* gives *Tl di*-m-*nitrophenyl nitrate*, decomp. >300°, also obtained from *m*-$C_6H_4(NO_2)_2$ H_3BO_3, and $TlCl_3$. $TlEt_2Cl$ with NaOEt yields *$TlEt_2$ ethoxide*, b.p. 101—102°/0·1 mm., m.p. 43—45°. The following were also prepared from TlX_3 and the appropriate compounds; *Tl(C_6H_4·OH-o)$_2$ bromide*, m.p. >340°, *Tl di*-2-*pyridyl chloride*, m.p. 288—291°, *$TlCl_3$,3C_5H_5N*, m.p. 148—150°, *$TlBr_3$,3C_5H_5N*, m.p. 113—115°, *$TlCl_3$,3 2-C_5H_4BrN*, m.p. 145—146°, *$TlCl_3$,3 2-$C_5H_4(NH_2)N$,3HCl*, m.p. 121—125° (decomp.), *$TlCl_3$,cysteine,HCl*, m.p. ~350° (decomp.), *Tl [C_6H_3(NMe)$_2$-p]$_2$ bromide*, m.p. >350°, *Tl di*-p-, m.p. >330°, and *di*-o-*anisyl bromide*, m.p. >330°. *p*-Li·C_6H_4·NMe_2 with $BBu^a(OH)_2$ gives p-*dimethylaminophenylboric acid*, m.p. 243—245° (decomp.), which with $TlCl_3$ yields a purple dye. The following *Tl* salts were prepared: 2 : 4 : 6-*trinitrobenzoate*, m.p. 160—163° (decomp.); *oxalate*, m.p. 315—320° (decomp.); *naphthalene*-2-, m.p. 234—236°, *benzene*-, m.p. 185—187°, *lauryl*-, m.p. 143—145°, and p-*toluenesulphinate*, m.p. 154—156°; *phenyl*-, m.p. 200—201° (*Tl*$_2$ salt, m.p. 317—320°), and *diphenyl-phosphonate*, m.p. 203—205°; salt of $MeNO_2$, decomp. from 160°; *salt* of $EtNO_2$, m.p. 80—82° (decomp.); *Me*, m.p. 136—140° (decomp.) *Et*, decomp. 100°, and *Bu^a sulphide*, m.p. 84—90° (decomp.); *thiophenoxide*, m.p. 258—260°, p-*thiotolyl-oxide*, m.p. 178—180°, *thio-β-naphthoxide*, m.p. 165—168°, and *terephthalate*, m.p. >340°. F. R. G.

IX.—PROTEINS.

Denaturation of tobacco mosaic virus by carbamide. I. Biochemistry. M. A. Lauffer and W. M. Stanley (*Arch. Biochem.*, 1943, **2**, 413—424; cf. A., 1939, III, 729).—Tobacco mosaic virus is transformed by 6M-$CO(NH_2)_2$ from a substance sol. in dil. aq. electrolytes into one insol. in such solvents. The denatured protein is readily sol. in 6M-, considerably less sol. in 4·5M-, and very slightly sol. in 3M-$CO(NH_2)_2$. It dissolves easily in very dil. aq. Na dodecyl sulphate and in 0·1M-NaOH, but not at all readily in 0·01M-NaOH. These changes are shown by means of osmotic pressure, high-speed quantity centrifugation, ultra-centrifugation, stream double refraction, and turbidimetric examination to be accompanied by disintegration of the high-mol. virus nucleoprotein particles into much smaller particles $\sim 10^4$ or 10^5. The nucleic acid is removed from the protein in this disintegration, and the no. of SH groups increases during denaturation. $CO(NH_2)_2$ also causes a loss of virus infectivity. Residual infectivity is always associated with remaining high-mol. nucleoprotein in cases of partial denaturation, and the sp. infectivity of this residual material is considerably < that of untreated virus. This shows that virus inactivation can occur before the virus nucleoprotein mol. is extensively disintegrated, and denaturation by $CO(NH_2)_2$ appears to involve at least two consecutive reactions. The overall denaturation process is irreversible.
J. N. A.

Effect of denaturation on sulphur content of ovalbumin and edestin. B. M. Hendrix and J. Dennis (*Arch. Biochem.*, 1943, **2**, 371—380).—Denaturation of ovalbumin with acid and alkali causes a decrease in the S content of the protein. Material rich in S is removed from the protein by these treatments, and denaturation appears to be accompanied by addition of H_2O to the protein. Alkali-denaturation of edestin resembles acid- and alkali-denaturation of albumin, whilst acid-denaturation of edestin differs from other acid- and alkali-denaturations in that no S is removed from the protein.
J. N. A.

Effect of dry grinding on properties of proteins. I. Native, denatured, and coagulated ovalbumin. H. R. Cohen (*Arch. Biochem.*, 1943, **2**, 1—8).—Dry grinding (ball mill at 100 r.p.m.) of cryst. and acid-denatured ovalbumin (**I**) produces insol. protein. Heat-denatured (**I**) gives some H_2O-sol. protein; the insol. fraction contains more S and less tyrosine and tryptophan than does cryst. (**I**). The rates of digestion by pepsin of the ground proteins are intermediate between those of cryst. and coagulated (**I**).
E. R. S.

Effect of dry grinding on properties of proteins. II. Casein. III. Gelatin. IV. Human, ox, and pig coagulated hæmoglobins. H. R. Cohen (*Arch. Biochem.*, 1943, **2**, 345—351, 353—355, 357—361).—II. When casein (**I**) is dry ground for 48 hr. a H_2O-sol. fraction is obtained, which contains more P and less tryptophan (**II**) than the unground (**I**); it is also attacked by rennin. The other H_2O-sol. fractions by successive 48-hr. periods of grinding all contain more P and less (**II**) than native (**I**), and they are all unaffected by rennin. There is very little difference in N content of any of the fractions. They all contain dialysable proteins, and are pptd. from aq. solution by picric, trichloroacetic, and phosphotungstic acids, $HgCl_2$, and 50% saturation with $(NH_4)_2SO_4$. They are not precipitinogenic but produce anaphylactic sensitisation in guinea-pigs. The insol. residue left after prolonged grinding is only slowly attacked by trypsin. The H_2O-sol. fractions are all digested much more readily, whilst that from the first grinding is hydrolysed at a greater rate during the first 45 hr. than is native (**I**). The total H_2O-sol. product is partly nutritionally deficient since it does not support growth of mice although they are maintained in good health and at relatively const. wt., whilst the insol. residue is just as effective as is unground (**I**). The mechanism of degradation of the protein mol. by grinding is discussed.

III. Dry grinding of gelatin converts it into a protein sol. in cold H_2O. Grinding for 7 hr. has no effect on the ability to gel, but there is a marked increase in solubility in H_2O at room temp., and the time for gelling is considerably increased. After grinding for 72 hr. the product no longer forms a gel. There is no increase in formol titration val. during grinding, which shows that there is no appreciable cleavage of peptide bonds.

IV. Dry grinding of coagulated human, ox, and pig hæmoglobins (**III**) produces H_2O-sol. fractions which contain varying amounts of Fe. They all give the benzidine reaction, and the fact that the hæmatin is sol. in H_2O shows that the prosthetic group is not removed from the protein constituent during grinding. The H_2O-sol. proteins contain dialysable protein; they are non-coagulable by heat and require 50% or more EtOH for pptn. They are pptd. by $HgCl_2$, picric acid, and $CCl_3{\cdot}CO_2H$, and by 50% saturation with $(NH_4)_2SO_4$. They are sol. in acids and alkalis, and do not give rise to precipitin antibodies and do not react with native (**III**) antisera. The N content decreases with successive fractions, and in the case of human (**III**) the amount of tyrosine decreases in each successive fraction, whilst with ox (**III**) the amount of tyrosine in each fraction is fairly const. Tryptophan is absent from the last fractions from human (**III**) and from one of the H_2O-sol. fractions from ox-(**III**). 79% of coagulated human (**III**) is converted into H_2O-sol. protein in 384 hr. For coagulated ox- and pig-(**III**) the corresponding vals. are 75% in 192 hr. and 32·5% in 96 hr. respectively. The H_2O-sol. fractions from human (**III**) contain at least 70% of dialysable N which shows that they are small mol. fragments. The H_2O-sol. fractions from the various (**III**) differ from native (**III**) mainly in the ultra-violet spectrum between 313 and 264 mμ. In this region there is considerably more absorption than with native (**III**).
J. N. A.

Methionine- and tryptophan-free casein hydrolysates. A. A. Albanese (*Science*, 1943, **98**, 46).—1 kg. of casein in refluxed for 20—23 hr. with 500 ml. of H_2SO_4 and 1 l. of H_2O, cooled to 80°, 200 ml. of 30% H_2O_2 added, and the mixture kept at room temp. for 24 hr. 2 l. of H_2O and 4 l. of 16% CaO suspension are added, and the mixture is kept overnight and filtered through a norite-precoated filter. The $CaSO_4$ is re-suspended in 2 l. of hot H_2O, filtered, and the filtrate and washings conc. in vac. at 50—60° to 2 l., neutralised with 50% H_2SO_4, and refiltered. 650 g. of tryptophan-free (not detected) and methionine-free (0·12—0·21% of the protein) hydrolysate are obtained.
E. R. R.

Etherification of hydroxyamino-acid residues in silk fibroin by dimethyl sulphate. A. H. Gordon, A. J. P. Martin, and R. L. M. Synge (*Biochem. J.*, 1943, **37**, 538—543).—Fibroin with Me_2SO_4 and N-NaOH is *O*-methylated; the max. degree of methylation obtainable corresponds to conversion of nearly all the tyrosine residues and about half the serine residues, suggesting the presence in fibroin of two types of serine residues, differing in accessibility to methylation.
F. O. H.

X.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Lignin esters of mono- and di-basic aliphatic acids. H. F. Lewis, F. E. Brauns, M. A. Buchanan, and E. B. Brookbank (*Ind. Eng. Chem.*, 1943, **35**, 1113—1117).—The prep. of lignin from soda black liquor from hardwood cooks by pptn. with CO_2 is described. Lignin esters are prepared by adding the acid chloride to a solution of lignin in C_5H_5N, and isolated by pouring into ice-H_2O. The esters of 17 monobasic aliphatic acids, ranging from acetic to stearic, and of succinic, adipic, suberic, azelaic, benzoic, *p*-toluenesulphonic, and phthalic acids were prepared and their m.p. and solubility data tabulated. In esters of monobasic acids, 3, 4, or 5 acyl groups are combined with each structural unit of lignin. The m.p., which are not sharp, decrease with increasing chain length of the acid group. These esters are sol. in $COMe_2$, dioxan, C_6H_6, and EtOAc; the solubility in MeOH and EtOH decreases and in Et_2O and light petroleum increases with increasing mol. wt. of the acid radical. Esters of dibasic acids have higher m.p. and are less sol.; this is attributed to attachment of the acid mol. to two neighbouring lignin chains forming a network structure. The stearic ester has possible industrial applications as a mould lubricant for wood plastics and for incorporation in inks and paints.
R. H. F.

Purification and properties of humulon. V. Salac and J. Dyr (*Gambrinus*, 1943, **4**, 253—255).—A solution in MeOH of the residue obtained by extracting lupulin with Et_2O and evaporating the solution was freed from myricin wax, and the humulon (**I**) pptd. by aq. $Pb(OAc)_2$. The Pb salt of the α-bitter acid (**II**) was extracted with 25% H_2SO_4 + 4 vols. of Et_2O, and (**I**) purified by the *o*-$C_6H_4(NH_2)_2$ method, followed by pptn. of a solution in MeOH with H_2O. The crystals had m.p. 63—64°, $[\alpha]_D^0$ −206·24° in MeOH, −212·53° in EtOH, −190·44° in Et_2O. With solutions in C_6H_{14} $[\alpha]_D^{20}$ was ∝ the concn. Dil. aq. $FeCl_3$ gave a violet-brown and dil. aq. $CuSO_4$ an emerald-green colour with a solution of (**II**) in EtOH. Polarimetric determinations of (**I**) from different hops gave lower vals. than pptn. with $Pb(OAc)_2$.
J. G.

Relationship of lupulin to the bitter constituents of hops. V. Salac and J. Dyr (*Gambrinus*, 1943, **4**, 255—258).—Crude β-bitter acid (**I**), obtained as fine needles by the evaporation at 30° in CO_2 of an extract of lupulon (**II**) in C_5H_{12}, was dissolved in MeOH; 2 days later, two layers [a syrupy liquid containing β-soft resin (**III**), and a milky upper layer containing fine needles of (**I**)] had separated. After recrystallisation (**I**) had m.p. 78—81°, but (**II**) remained amorphous; both had [α] 0. Aq. $FeCl_3$ produced a brown and aq. $CuSO_4$ a blue-green colour with the MeOH solution. The crystals of (**II**) and their solutions in MeOH had no bitter taste, but (**III**) was very bitter. A dil. solution of lupulin in MeOH–H_2O boiled free from MeOH became very bitter owing to the rapid conversion of (**II**) into (**III**). Since [α] of hop oil is ~0, humulon can be determined polarimetrically (see above).
J. G.

Esters of penicillin.—See A., 1944, III, 141.

Purification and properties of penatin.—See A., 1944, III, 141.

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A II—Organic Chemistry.

MARCH, 1944.

I.—ALIPHATIC.

Catalytic isomerisation of saturated hydrocarbons.—See B., 1944, II, 2.

Production of branched-chain alkanes.—See B., 1944, II, 30, 31.

Production of *iso*octane.—See B., 1944, II, 2.

Reaction of unsaturated molecules with sodium platinichloride. A. Gelman (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **31**, 761—764).—Na_2PtCl_6 is reduced by CO, butadiene, or C_2H_4, to Na_2PtCl_4. Removal of the excess of Na_2PtCl_6 and then treatment with C_5H_5N gives the *compounds*, $C_5H_5N,H[PtCl_3{\cdot}CO]$, $[PtCl_2(C_4H_6)(C_5H_5N)]$, and $[PtCl_2(C_2H_4)(C_5H_5N)]$, respectively. Little, if any, reaction occurs with NO. R. S. C.

γδ-Diethyl-Δ$^{\gamma}$-hexene and γδ-diethylhexane. Preparation and properties. H. Koch and F. Hilberath (*Ber.*, 1940, **73**, [*B*], 1171—1173).—$CEt_2(CO_2Et)_2$ passes in presence of Na and EtOH under H_2 at 250°/70 atm. into $CHEt_2{\cdot}CO_2Et$, converted by MgEtBr into γδ-diethylhexan-γ-ol. This is dehydrated by $H_2C_2O_4$ at 110° to a mixture of much *γδ-diethyl-Δ$^{\gamma}$-hexene* (**I**) and little -Δ$^{\beta}$-hexene which are readily separated from one another by fractional distillation. (**I**) has b.p. 158·10°/758·0 mm., 157·85°/754 mm., and 158·2° (corr.)/760 mm. Oxidation with $KMnO_4$ or $Pb(OAc)_4$ affects the side-chains exclusively and ozonisation followed by catalytic hydrogenation takes an abnormal course, probably by reason of the inertia of the double linking and the unusual readiness of substitution. For this reason correct I vals. are obtained only by the I–CNS method. The results with ICl (Wijs) or NaBr–Br solution are 25% and 110% high whereas those with ICl in MeOH saturated with $CaCl_2$ are very low. (**I**) is not hydrogenated in abs. EtOH containing PtO_2 at atm. pressure but passes smoothly in presence of Pd–C into *γδ-diethylhexane*, b.p. 160·7°/760 mm.; this gives an uninvestigated cryst. product when irradiated in presence of Br. H. W.

Hydration of olefines.—See B., 1944, II, 3.

Hydroxylation of unsaturated halides.—See B., 1944, II, 3.

Recent developments in nitroparaffins.—See B., 1944, II, 29.

Purification of pentaerythritol.—See B., 1944, II, 31.

Phosphates. III. Phosphatase models. M. Lora Tamayo and F. Segovia (*Anal. fís. quím.*, 1943, **39**, 382—395).—$Mg^{\cdot\cdot}$ accelerates the trans-esterification of Na β-glycerophosphate by MeOH, and the catalysis by $CH_2Bz{\cdot}OH$ of the hydrolysis of Et phenylphosphate (**I**). Hydrolysis of (**I**) is slightly catalysed by $OH{\cdot}CH_2{\cdot}CO{\cdot}NHPh$ but Mg is without effect. F. R. G.

Long-chain acids containing a quaternary carbon atom. II. N. Polgar and (Sir) R. Robinson (*J.C.S.*, 1944, 615—619).—*α-Ethyl-α-decyltetradecoic acid* (**I**) has been synthesised by the method of Hudson *et al.* (A., 1942, II, 130) and found to differ from phthioic acid (**II**) (cf. Stenhagen *et al.*, A., 1941, II, 331). It appears probable that the chain in (**II**) must be longer than thought possible heretofore on *X*-ray evidence. Any structure with two long chains of comparable length will probably be found inconsistent with the small area of the compressed films of (**II**). Hence there is probably only one long chain and the smaller apparent length is due to the considerable tilting of the mols. $n\text{-}C_{10}H_{21}{\cdot}CH(CO_2Et)_2$ is transformed into $n\text{-}C_{10}H_{21}{\cdot}C(C_{12}H_{25})(CO_2Et)_2$, which yields α-decyl-*n*-tetradecoic acid (**III**), m.p. 47° (amide, m.p. 112·5°); the Me ester, b.p. 198—200°/0·25 mm., is transformed by CPh_3Na and MeI followed by alkaline hydrolysis into *α-methyl-α-decyl-n-tetradecoic acid* (**III**), m.p. 41° rising to 44·5° in 8 months (corresponding *amide*, m.p. 42°). It could not be resolved into its optical antipodes by quinine, cinchonine, strychnine, or brucine. *α-Ethyl-α-decyl-n-tetradecoic acid*, m.p. 27—28° rising to 31° in a few weeks (*amide*, a viscous oil), is prepared similarly. The Me ester of α-n-*heptyl*-n-*hexadecoic acid*, m.p. 42°, is transformed analogously into *α-methyl-α-n-heptylhexadecoic acid*, m.p. 44° (*amide*, m.p. 30—31°). *α-n*-Heptylnonoic acid, m.p. 26—27°, obtained from $n\text{-}C_7H_{15}Br$ and $CH_2(CO_2Et)_2$, is transformed through the Me ester into *α-methyl-α-heptylnonoic acid*, a viscous liquid, b.p. 171—171·5°/0·2 mm. (*amide*, a very viscous oil, b.p. 181—182°/0·2 mm.). $COMe{\cdot}C_9H_{19}$ and $C_{12}H_{25}{\cdot}MgBr$ afford mainly *methyl-n-nonyl-n-dodecylcarbinol*, b.p. 200—204°/~0·2 mm. $CH_2(CO_2Et)_2$, *sec.*-$C_{11}H_{23}Br$, Na, and some NaI in boiling EtOH yield Et_2 *sec.*-undecylmalonate, b.p. 180—182°/18 mm., converted into Et_2 sec.-*undecyl-n-dodecylmalonate*, b.p. 210—212°/0·16 mm., hydrolysed by boiling KOH–Pr$^{\alpha}$OH and then decarboxylated to *β-methyl-α-n-dodecyl-lauric acid*, b.p. 228—230°/0·3 mm. (*amide*, m.p. 102—103°). (**III**) is converted by successive treatments with $SOCl_2$ and CH_2N_2 in Et_2O into the corresponding diazo-ketone, which with a hot suspension of Ag_2O in MeOH yields Me *β-n*-decyl-*β-n*-dodecylpropionate, b.p. 212—214°/0·25 mm., hydrolysed to the *acid*, m.p. 0° rising after several weeks to 26·5° (*amide*, m.p. 55°). β-Methyl-α-*n*-dodecyl-lauric acid is converted through the chloride and diazo-ketone into the Et ester of *γ-methyl-β-n-dodecyltridecoic acid*, b.p. 209—210°/0·1 mm. (non-cryst. *amide*). (**IV**) passes through the chloride into the diazo-ketone, m.p. 36°, which gives *Me β-methyl-β-decylpentadecoate*, b.p. 196—197°/0·2 mm.; the *acid*, a viscous liquid, furnishes a non-cryst. *amide*. $(n\text{-}C_{10}H_{21})_2CO$, Zn filings, and $CH_2Br{\cdot}CO_2Et$ in boiling C_6H_6–Et_2O yield an undistillable product, converted by $SOCl_2$ in C_5H_5N followed by H_2O at 0° into *Et β-decyl-Δ$^{\alpha}$-tridecenoate*, b.p. 192—196°/0·4 mm.; this is hydrogenated (Raney Ni) at 40—60°/60 atm. to Et β-decyltridecoate, b.p. 179—181°/0·2 mm., which is reduced (Na–Bu$^{\alpha}$OH–light petroleum) to *γ-decyltridecanol*, b.p. 163—165°/0·15 mm. The corresponding iodide and $CHNa(CO_2Et)_2$ afford Et_2 *γ-decyltridecylmalonate*, b.p. 221—224°/0·45 mm., transformed by Na and MeI followed by hydrolysis and decarboxylation into *α-methyl-δ-decylpentadecoic acid*, which becomes turbid at 0°. H. W.

Purification of maleic anhydride.—See B., 1944, II, 3.

Production of glutaric acid.—See B., 1944, II, 3.

New reaction of ethylene oxide. V. Condensation of ethylene oxide with cyclic β-keto-esters. K. G. Pakendorf and F. F. Matschus (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **31**, 441—443).—Et *cyclo*pentanone-2-carboxylate and $(CH_2)_2O$, with piperidine at room temp. for 20 days, give *α-(γ'-carbethoxypropyl)-γ-butyrolactone*, b.p. 172—174°/6 mm. Me 6-methyl*cyclo*hexanone-2-carboxylate similarly gives *α-(δ'-carbomethoxy-n-amyl)-γ-butyrolactone*, b.p. 175°/6 mm. The mechanism suggested is the alcoholysis of the spirocyclic lactones first formed. S. A. M.

Separation of aldehydes and ketones.—See B., 1944, II, 4.

Stabilisation of unsaturated ketones.—See B., 1944, II, 32.

Manufacture of tertiary amines.—See B., 1944, II, 32.

Rotatory dispersion of α-amino-acids. J. W. Patterson and W. R. Brode (*Arch. Biochem.*, 1943, **2**, 247—257).—Measurements of the rotatory dispersion for λ 4400 to 6600 mμ. of 14 NH_2-acids, their hydrochlorides, and Na salts are employed to determine configuration. Simple rules are given for assigning configuration to α-NH_2-acids which are based on examination of rotatory dispersion curves. W. McC.

Complexes of zinc and glycine.—See A., 1944, I, 67.

Organic catalysts for the elimination of carbon monoxide from formamide. III. Catalysts with phenolic hydroxyl as active group. T. Enkvist [with A. Kurkela] (*Ber.*, 1940, **73**, [*B*], 1253—1258; cf. A., 1940, II, 71).—In presence of alkali, compounds with phenolic OH accelerate the elimination of CO from $HCO{\cdot}NH_2$ more markedly than the corresponding catalysts with alcoholic OH. PhOH is nearly as potent as the most efficient catalysts (sucrose; $OH{\cdot}CH_2{\cdot}CO{\cdot}NHPh$) with alcoholic OH. The catalytic effect of phenols can be increased by suitable substituents, the position of which frequently has a very decisive influence. In *o-* and *p*-cresol Me is weakly activating, scarcely so in *m*-cresol, and restrictive in orcinol. C_5H_{11} and Pr$^{\beta}$ do not activate. In *o-* and *p*-positions Ph activates slightly but a second C_6 nucleus as in $C_{10}H_8$ has no noticeable effect. Cl is indifferent or inactivating. NH_2 is at most slightly inactivating, strongly inactivating, or indifferent accordingly as it is in the *o-*, *m-*, or *p*-position. NMe_2 and NEt_2 are distinctly inactivating in the *m*-position. OMe and $\cdot CH(OH){\cdot}CH_2{\cdot}NHMe$ are indifferent. NO_2, NO, $N_2{\cdot}SO_3H$, $\cdot CH_2{\cdot}CH(NH_2){\cdot}CO_2H$, and $\cdot CH{:}NPh$ are inactivating, as also is the substitution of

C_5H_5N for C_6H_6. CO_2H is usually inactivating but can be indifferent. In the cases investigated ·CO·NHPh is inactivating. OH in *ortho-* or *vic*-position causes strong activation [*o*-$C_6H_4(OH)_2$; 3 : 4 : 1-$(OH)_2C_6H_3$·CO_2H; adrenaline, 1 : 2 : 3-$C_6H_3(OH)_3$]; in the *p*-position (quinol) activation is less pronounced, whereas in the *m*-position (resorcinol; orcinol), *sym.* [1 : 3 : 5-$C_6H_3(OH)_3$] and *as.* [1 : 2 : 4-$C_6H_3(OH)_3$] positions there is slight or marked inactivation increasing to complete inhibition with 1 : 3 : 5-$C_6H_3(OH)_3$. In the following points the catalysts do not appear to conform with Langenbeck's rules (A., 1940, I, 326). With different substituents there appears to be no definite position causative of activation or inactivation. One and the same substituent can be activating or inactivating according to its position; this is true in particular for OH and less so for Me. Not only all substituents of the second order (CO_2H, NO_2, NO, SO_3H) but also certain typical members of the first order (NH_2, Cl) are inactivating. The reactions are discussed.

H. W.

Properties of urea, biuret, and triuret. R. C. Haworth and F. G. Mann (*J.C.S.*, 1944, 603—606).—Biuret (**I**) (38%), m.p. 190°, and triuret, $CO(NH·CO·NH_2)_2$ (15%), m.p. 231—232°, are best prepared from $CO(NH_2)_2$ (**II**) and $SOCl_2$. Under controlled conditions (**II**) and SO_2Cl_2 give the *substance*, $C_4H_{16}O_7N_8S$, but on heating cyanuric acid (**III**) with $ClSO_3H$ (0·5 mol.) it gives (**I**), with 1·0 mol. it gives (**III**) or $NH_2·SO_3H$ according to conditions. The properties of (**II**) are the converse of those of $CS(NH_2)_2$ (**IV**) in that H_2O cannot be abstracted from (**II**), but H_2S is readily eliminated from (**IV**), whilst NH_3 is readily lost from (**II**) but not from (**IV**). (**I**) may exist as a resonance hybrid between the normal form and several zwitterion forms, or may be partly or fully enolised. The peculiarities of (**I**) are discussed. (**III**) with $CaCl_2$ and NH_3 gives (?) *Ca cyanurate trihydrate.*

H. M. C.

Co-ordination number of bivalent lead.—See A., 1944, I, 68.

Preparation of thioamides.—See B., 1944, II, 4.

***ψ*-Halogens. XXXV. Solid and liquid thiocyanic acid.** L. Birckenbach and E. Büchner [with K. Kraus and, in part, E. Kayser] (*Ber.*, 1940, **73**, [*B*], 1153—1168).—HCNS cannot be prepared by the action of HCl or HF on an alkali thiocyanate but is obtained pure from KCNS and $KHSO_4$ by a modification of the method of Rück *et al.* (A., 1912, i, 954). The vapours condense in liquid air to colourless, enamel-like *thiocyanic acid* (**I**), m.p. −110° (vac.) (lit. m.p. 5°). When cautiously warmed it melts to a completely colourless, transparent, mobile liquid which solidifies at −110° to colourless (**I**), which again gives a colourless molten mass if the temp. of warming is −100°. The solidifying point is determined at −110° from the cooling curve. Slow warming of (**I**) causes formation of individual crystals at ~−90° and between −90° and −85° solidification to a *polymer* (**II**) although it is sometimes possible by very careful warming and avoidance of all agitation to keep small quantities of substance as liquid up to −50° or over. Generally at −55° to −50° (**II**) undergoes decomp. with (in vac.) formation of a *substance* (**III**) of ivory or pale yellow colour which darkens towards 0°. If a good vac. is maintained during slow warming the product can be kept for days in a vac. at room temp. If the amount is not too great, this can be almost completely depolymerised in a high vac., volatilisation being accompanied by absorption of much heat. This behaviour combined with analytical results (determinations of mol. wt. are impossible) allies (**III**) with cyanuric acid and causes it to be regarded as a trimeride "thiocyanuric acid." (**I**), (**II**), and (**III**) can be kept pure only in a vac. since even in the cold they evolve HCNS vapour which decomposes in the warmer parts of the apparatus and thus induces impurities. In the rectification of larger amounts of substance between −110° and −40° these parts must be cooled in CO_2–Et_2O at −50° to −40°. If (**III**) is allowed to warm to room temp. in a closed vessel filled or not filled with dry air but without pumping off the gas it darkens slowly to dark brown or red and at 3° a rapid change occurs with considerable evolution of heat, foaming, and formation of a paste (**IV**); this is accompanied by slight decomp. into HCN and S (this temp. has been incorrectly regarded as the m.p.). The non-volatility, apparently amorphous state, and sparing solubility of (**IV**) cause it to be regarded as a hexameride although attempted determinations of mol. wt. were unsuccessful. The heating curve of (**I**) shows breaks at −110°, −92° (between −92° and −89°), at −50° to −49°, and at 0° becoming more pronounced at 3°. Measurements of v.p. give similar results but give the impression that a homogeneous system is not under investigation. The structure H·NCS is assigned provisionally to (**I**).

H. W.

Production of nitriles.—See B., 1944, III, 33.

System hydrocyanic acid–diethyl ether. L. Birckenbach and E. Büchner (*Ber.*, 1940, **73**, [*B*], 1168—1171).—The m.p. diagram of mixtures of HCN and Et_2O proves the formation of an additive *compound* (1 : 1), m.p. −87°. Its stability is small. It does not exist in the vapour phase. HCN and Et_2O give a eutectic mixture at −121·5° to −121·6°.

H. W.

II.—SUGARS AND GLUCOSIDES.

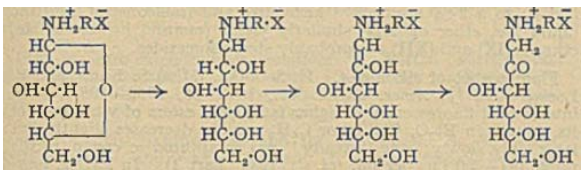
Calcium chloride compounds of *D*-α-glucoheptose (*D*-glycero-*D*-guloaldoheptose). H. S. Isbell and H. L. Frush (*J. Res. Nat. Bur. Stand.*, 1943, **3**, 163—168).—In support of the concept that sugars having like configurations for the atoms comprising the pyranose ring have like properties, it has been found that *D*-glycero-*D*-guloaldoheptose (**I**) (formerly *D*-α-glucoheptose) resembles *D*-gulose in that it forms cryst. compounds with $CaCl_2$ and that the equilibrium which exists in aq. solutions is shifted markedly by changes in [$CaCl_2$], addition of which shifts the equilibrium towards the unknown α-pyranose modification. The equilibrium optical rotation of (**I**) in 4% aq. solution in presence of $CaCl_2$ varies according to $[\alpha]_D^{20} = -20·2 + 3·54m - 0·067m^2$, where m = g. of $CaCl_2$ in 100 mols. of solution. The cryst. *compound*, (**I**),$CaCl_2$,$2H_2O$, mutarotates in 4% aq. solution in accordance with $[\alpha]_D^{20} = -6·5 \times 10^{-0·607t} - 9·3°$.

H. W.

The cardiac glucosides. W. E. Bouman (*Pharm. Tijds. Nederl.-Indie*, 1941, **18**, 39—48, 65—75, 97—104, 130—137, 177—187).—A review.

***N*-Glycosides. II. Amadori transformations.** F. Weygand (*Ber.*, 1940, **73**, [*B*], 1259—1278; cf. A., 1940, II, 69).—Glycosides of primary aromatic amines are readily obtained by heating 1 mol. of sugar with 1·1—1·4 mols. of amine and 2—4 mols. of H_2O. Only those derived from glucose are converted into *iso*amines when melted or heated in MeOH or EtOH. Surprisingly, pure *p*-phenetidine-*d*-glucoside (**I**) is not isomerised in EtOH. Apparently identical experiments in which glucose, *p*-OEt·C_6H_4·NH_2, and H_2O are heated at 100° lead sometimes to (**I**) and sometimes to *d-iso*glucose-*p*-phenetylamine (**II**) so that it is doubtful if (**II**) is formed through (**I**). Addition to the mixture of increasing amounts of HCl leads to the isolation of (**II**) (the glucosides of *p*-toluidine, *p*-OMe·C_6H_4·NH_2, and *o*-4-xylidine behave similarly) in very greatly improved yield, small amounts of acid increasing both the rate of glucoside formation and isomerisation. Larger amounts of acid rapidly cause darkening. The prep. of piperidine-*d*-glucoside, m.p. 129—130°, and sulphanilamide-*d*-glucoside, m.p. 207—208°, from the sugar, amide, H_2O, and a little HCl is described. The prep. of the following under varied conditions is described: *d-iso*glucose-*p*-tolylamine (**III**), m.p. 153—154°, from glucose or mannose; *d-iso*glucose-*p*-phenetylamine, m.p. 154°; d-iso*glucose*-p-*anisylamine*, m.p. 140—141°, and *d-iso*glucose-3 : 4-dimethylphenylamine, m.p. 161—162°. (**III**) is reduced by Na–Hg in H_2O to *p*-tolyl-*d*-mannamine, m.p. 195—196°. In acid solution in which they form salts the catalytic hydrogenation (PtO_2) of the *iso*sugaramines affects preferentially the aromatic nucleus and the CO group of the side-chain remains intact. In neutral solution the results are variable whereas in alkaline solution reduction occurs generally in the side-chain, whereby 1 mol. of the *iso*amine absorbs exactly 1 H_2. A method of determining *iso*amine in solution is thus afforded. The following are thus produced: 3 : 4-dimethylphenyl-*d*-mannamine, m.p. 185—186°, $[\alpha]_D^{20}$ +21·4° in C_5H_5N; p-*anisyl*-d-*mannamine*, m.p. 191—192°, $[\alpha]_D^{20}$ +27·8°. Xylose, *p*-toluidine, H_2O, and AcOH at 75° rapidly yield *p*-toluidine-*d*-xyloside, further converted into *d-iso*xylose-*p*-tolylamine, which could not be obtained cryst. It is converted into d-*lyxose*-p-*tolylamine*, m.p. 156—158°, $[\alpha]_D^{19}$ +26°, when hydrogenated (PtO_2) in EtOH containing the acid used in the isomerisation or in alkaline solution at 20° or 4° but not at 58°. Non-cryst. *l-iso*arabinose-*p*-tolylamine is obtained from *l*-arabinose (**IV**), *p*-toluidine, H_2O, and AcOH and identified by hydrogenation to the expected epimerides, l-*arabinose*-p-*tolylamine* (**V**), m.p. 178—179°, $[\alpha]_D^{19}$ −7·1°, and l-*ribose*-p-*tolylamine*, m.p. 140—141°, $[\alpha]_D^{19}$ +31° in C_5H_5N. (**V**) is obtained also by reduction of *p*-toluidine-*l*-arabinoside (Ni in aq. MeOH; H_2 at 90°/50 atm.). (**IV**), *o*-4-xylidine, H_2O, and HCl afford *l-iso*arabinose-3 : 4-dimethylphenylamine, hydrogenated (PtO_2 in EtOH containing acid at 10°) to *l*-arabinose-3 : 4-dimethylphenylamine, m.p. 138—139°, $[\alpha]_D^1$ −12·3°, in neutral solution to l-*ribose*-3 : 4-*dimethylphenylamine*, m.p. 143°, $[\alpha]_D$ +30° in C_5H_5N, also obtained in alkaline solution. *d*-Arabinose is converted into *d-iso*arabinose-3 : 4-dimethylphenylamine, hydrogenated in alkaline solution at 20° to d-*ribose*-3 : 4-*dimethylphenylamine*, m.p. 142°, $[\alpha]^{22}$ −31·4°, identical with the substance obtained from *o*-4-xylidine-*d*-riboside. Under the new conditions *p*-toluidine-*l*-rhamnoside is isomerised to l-*rhamnose*-p-*tolylamine*, m.p. 183—184°, $[\alpha]_D^{20}$ −19·7° in C_5H_5N. Aniline-*d*-glucoside in presence of H_2O or a little acid is isomerised to the non-cryst. *d-iso*glucosephenylamine, which strongly reduces cold, alkaline solutions of *o*-$C_6H_4(NO_2)_2$ and is hydrogenated in alkaline solution to *d*-mannosephenylamine, m.p. 175—176°, showing that the Amadori isomerisation, impossible under the older conditions, has actually occurred. *d-iso*Glucose-*p*-tolylamine is obtained by Amadori isomerisation not only from *p*-toluidine-*d*-glucoside but also from *p*-toluidine-*d*-mannoside. In cases in which the *iso*amines can be obtained from two epimeric glycosides it is proposed to name the *iso*-compound from the sugar which is commonest in nature or in the case of the rare sugars from that with which isomerisation is first effected. The successful isomerisation of *p*-tolu-

idine-*d*-galactoside is shown by the subsequent hydrogenation to d-*galactose*-p-*tolylamine*, m.p. 180—181°, $[\alpha]_D^{21}$ −13·6° in C_5H_5N. The mechanism of the Amadori isomerisation is formulated thus (R = C_6H_4Me):



If isolation of the glucosides of primary amines is desired it is generally necessary to work without addition of acid although if the Amadori isomerisation occurs slowly acids or H salts may be added if the reaction is interrupted sufficiently soon. A suitable division of the glycosides is sketched. For the prep. of *N*-polyhydroxylalkyl derivatives by hydrogenation (at 80—100°/high pressure) of *N*-glycosides complete absence of acid is necessary if the hydrogenation product is to be free from epimeric compounds. The formation of (*d*-arabo)tetrahydroxybutylquinoxaline from *o*-$C_6H_4(NH_2)_2$ and *d*-glucose in slightly acid solution is readily explained if the incidence of an Amadori isomerisation is admitted. In the biogenesis of lactoflavin it is possible that the ribityl residue in a preliminary stage enters the flavin mol. by an Amadori isomerisation from either an *N*-*d*-riboside or *N*-*d*-arabinoside. The CO group at $C_{(2)}$ must be reduced to CH·OH with formation of the *d*-ribityl configuration. H. W.

***N*-Glycosides. III. Steric course of the hydrogenation of *iso*-glucosamines. Rules of rotation with 9-polyhydroxyalkylflavines and *N*-polyhydroxyalkylbenzenes.** F. Weygand (*Ber.*, 1940, **73**, [*B*], 1278—1283).—In acid solution, only *l*-arabinose-3 : 4-dimethylphenylamine is isolated by the hydrogenation of *l*-*iso*arabinose-3 : 4-dimethylphenylamine whereas at 20° in presence of EtOH–alkali the only isolable product is the *l*-ribamine derivative. It is not impossible that the epimerides are formed in small proportion. Hydrogenation of *iso*glycosamines in alkaline solution, *i.e.*, in the enolic form, is an addition of H_2 at an ethylenic linking which occurs in the *cis*- or *trans*-position according to the rate of hydrogenation and to the catalyst employed. Since the ethylenic compound can occur in a maleinoid and fumaroid form varying proportions of epimeric compounds are to be expected according to the form which is present and the mode of addition. The sense of rotation of the 9-polyhydroxyalkylflavines for the *D* line depends solely on the configuration at $C_{(\beta)}$. If in Fischer's projection (·CH_2·OH group below; ·CH_2·N: group above) the OH at $C_{(\beta)}$ of the polyhydroxyalkyl chain projects to the right, the rotation in 0·1N-NaOH is negative and conversely. Similarly for *N*-polyhydroxyalkylbenzenes if in Fischer's projection (·CH_2·OH group below; ·CH_2·NHR group above) the OH at $C_{(\beta)}$ of the polyhydroxyalkyl chain projects towards the right, the rotation in C_5H_5N is negative and conversely. H. W.

Karakin, glucoside of *Corynocarpus lævigata*, and hiptagenic acid. C. L. Carter (*J.S.C.I.*, 1943, **62**, 238—240).—Karakin, a constituent of karaka nuts, closely resembles hiptagin in chemical properties, but from lack of a specimen of hiptagin the exact relationship cannot be established. Their common hydrolytic product, hiptagenic acid, is believed to be the oxime of aldehydroglyceric acid, OH·N:CH·CH(OH)·CO_2H. A second hydrolytic product of karakin is aminoglucose or aminomannose.

Amylolytic degradation of starch. W. N. Haworth, H. Kitchen, and S. Peat (*J.C.S.*, 1944, 619—625).—It is shown that β-amylase (**I**) hydrolyses the amylopectin component of starch with the formation of maltose and a limit dextrin, dextrin-*A* or α-amylodextrin (**II**) (40 wt.-% of original starch). End-group assay shows (**II**) to have an apparent unit chain length of 11—12 glucose units. (**II**) is not susceptible of further attack by (**I**) until it has been "sensitised" by contact with salivary amylase. The action of (**I**) then continues until a second resting stage is reached, viz., dextrin-*B* (**III**) [38% of (**II**), 7—8 glucose units]. (**III**) is not further hydrolysed by (**I**), nor sensitised by saliva, but is hydrolysed by salivary amylase to dextrin-*C* (**IV**) [67% of (**III**); 5—6 glucose units] and maltose. (**IV**) is slowly hydrolysed by pancreatic amylase to dextrin-*D* (**V**) [80% of (**IV**); 4—5 glucose units] and a sugar. Properties of (**II**)—(**V**) are given. The mechanism of amylolysis is explicable on the basis of the simple laminated formulation of the structure of starch of Haworth *et al.* (A., 1937, II, 232) if it be assumed (i) that the impediment to the action of (**I**) is represented by the polymeric link which unites the unit chains; (ii) that the polymeric links are ruptured by an enzymic constituent of saliva and of malt α-amylase; and (iii) that the unit chains so liberated immediately recombine with the formation of new polymeric (1 : 6-α-glucosidic) links with a different orientation of position on the respective chains. It is not necessary to postulate a complex, highly ramified structure for amylopectin, such as that proposed by Meyer (A., 1940, II, 268), to explain the facts of amylolysis. H. M. C.

III.—HOMOCYCLIC.

Cracking of *cyclo*hexane; thermal and catalytic decomposition at high pressures.—See B., 1944, II, 1.

Preparation and absorption spectra of five pure carotenoid pigments. F. P. Zscheile, J. W. White, jun., B. W. Beadle, and J. R. Roach (*Plant Physiol.*, 1942, **17**, 331—346).—Methods of purifying α- and β-carotene, cryptoxanthol, luteol, and zeaxanthol are described, absorption spectra in the range 3800—5300 A. are determined. A. G. P.

Catalytic alkylation of aromatic hydrocarbons.—See B., 1944, II, 4.

Production of benzylsulphonyl chlorides.—See B., 1944, II, 33.

Mechanism of inhibition of styrene polymerisation.—See A., 1944, I, 66.

Mechanism of addition polymerisation. Kinetics and elementary steps of polyreactions. Rate theory and some physical and chemical properties of high polymers.—See A., 1944, I, 65.

Exchange reactions of lithium phenyl. IV. Production of diphenyl from fluorobenzene and lithium phenyl. G. Wittig, G. Pieper, and G. Fuhrmann (*Ber.*, 1940, **73**, [*B*], 1193—1197).—Under identical conditions LiPh reacts with PhI, PhBr, PhCl, and PhF in Et_2O to the extent of 5, 7, 5, and 75%, respectively. The greatly superior reactivity of PhF is due to the strongly electronegative nature of F which polarises the *o*-CH linking more strongly than the other halogens and thus facilitates replacement of H by Li. Entry of the metal polarises the C–F linking and thus increases the reactivity of F. Evidence in favour of this view is found in the production of *o*-C_6H_4Ph·CPh_2·OH (converted by AcOH into 9 : 9-diphenylfluorene) by the action of $COPh_2$ on the product from PhF and LiPh. F appears superior to OMe in polarising action. In practice the change appears somewhat more complex and a scheme is discussed according to which it is impossible to obtain diphenyls in 100% yield from halogenobenzenes and LiPh or other metallic phenyl. With *o*- and *p*-$C_6H_4Br_2$ the production of diphenyls $C_6H_4Br_2$ + LiPh → LiBr + C_6H_4PhBr is overshadowed by halogen–metal interchange, C_6H_4Br·Br LiPh → Li·C_6H_4Br + PhBr. In the reactions of PhF further evidence is found in favour of the view that alkali-org. compounds are intermediates in the elimination of HHal from AlkHal and alcoholic alkali, EtBr → K·$[CH_2]_4$·Br → CH_2:CH_2 + Br, and in displacements of the ethylenic linking, CH_2Ph·CH:CH_2 → CHPhK·CH:CH_2 → CHPh:CH·CH_2K → CHPh:CHMe. H. W.

Polymerisation of 1 : 2-dihydronaphthalene and polymer.—See B., 1944, II, 4.

Preparation of 1- and 2-methylnaphthalenes from tar oil fractions. II. 1-Methylnaphthalene.—See B., 1944, II, 1.

Preparation of 2 : 3-dinitronaphthalene and 3-nitro-2-naphthylamine. H. H. Hodgson and H. S. Turner (*J.C.S.*, 1944, 635—636).—3 : 1-NO_2·$C_{10}H_6$·NHAc is nitrated (HNO_3) to 2 : 3-*dinitro*-1-*naphthylamine*, m.p. 160—161°, deaminated to 2 : 3-$C_{10}H_6(NO_2)_2$, m.p. 159°. This is reduced to 3-*nitro*-2-*naphthylamine*, m.p. 86·5° (*Ac* derivative, m.p. 191·5—192·5°), by hydrated Na_2S. NN′-*Di*-p-*toluenesulphonyl*-1 : 4-*naphthylenediamine*, m.p. 249—250°, could not be nitrated and 2 : 3 : 1 : 4-$(NO_2)_2C_6H_2(NH_2)_2$ could not be deaminated. H. M. C.

Derivatives of sulphanilamide.—See B., 1944, III, 16, 17.

Complex formation and rearrangement of *p*-hydroxylaminobenzenesulphonamide. H. Burton and N. Walker (*J.C.S.*, 1943, 656—657; cf. A., 1941, II, 220).—Confirmatory evidence is given that *b*-OH·NH·C_6H_4·SO_2·NH_2 (**I**), m.p. 140°, and *p*-NH_2·C_6H_4·CO_2·NH_2 (**II**) form a 2 : 1 complex (**III**), m.p. 161·5° (cf. Sevag, A., 1943, II, 158). (**II**) can be isolated after removal of (**I**) [as azoxybenzene-4 : 4′-disulphonamide (**IV**)] by air oxidation of (**III**) in dil. aq. NH_3 at room temp. After acetylating (**III**) by Ac_2O at room temp., the respective Ac derivatives of (**I**) and (**II**) are isolable (from MeOH). (**III**) is prepared from its components in H_2O. (**I**) and 5% aq. HCl or H_2SO_4 (in CO_2) at 100° (bath) give (**IV**) and *p*-NH_2·C_6H_4·OH (**V**); (**III**) similarly yields (**IV**), (**V**), and (**II**). A. T. P.

Derivatives of *p*-aminobenzenesulphonanilide.—See B., 1944, II, 4.

Preparation and properties of certain poly-sulphanilamide compounds. F. G. Mann and J. Watson (*J.C.S.*, 1943, 606—609).—*p*-NHAc·C_6H_4·SO_2Cl (**I**) and 10% aq. NaOH, added successively in very small quantities to aq. $C(CH_2$·$NH_2)_4$ at 45—50°, at great dilution, give *tetra*-(p-*acetamidobenzenesulphonamidomethyl*)*methane*, m.p. 304—306°, hydrolysed by boiling dil. HCl to the $(NH_2)_4$-derivative, m.p. 243·5—244°. Similarly, $N([CH_2]_2$·$NH_2)_3$ affords *tri*-(β-p-*acetamidobenzenesulphonamidoethyl*)*amine*, m.p. 198·5—200·5° (softens at 115°), and thence *tri*-(β-*sulphanilamidoethyl*)*amine*, m.p. 178·5—180° (decomp.). The analogous sulphonamido-derivative

from $N([CH_2]_3\cdot NH_2)_3$ could not be prepared. $OH\cdot CH(CH_2\cdot NH_2)_2$ gives, through the Ac_2 derivative, m.p. 232·5—233·5°, *βγ-di(sulphanilamido)isopropyl alcohol*, m.p. 177—179°. $NH_2\cdot CH(CH_2\cdot NH_2)_2$ yields *αβγ-tri(sulphanilamido)propane*, m.p. 234·5—236° (decomp.) (softens at 220°) (Ac_3 derivative, m.p. 218·5—220·5°). *NN'-Di-(p-acetamidobenzenesulphonyl)-NN'-di-(β-p-acetamidobenzenesulphonamidoethyl)ethylenediamine*, m.p. 290·5—291·5°, and thence the $(NH_2)_4$-derivative, m.p. 208—209°, are obtained from $(CH_2\cdot NH\cdot[CH_2]_3\cdot NH_2)_2$ and (**I**) in C_5H_5N. No antimalarial activity is noted with the compounds. A. T. P.

***p*-Substituted benzenesulphonyldiguanides.**—See B., 1944, II, 5.

Mechanism of the diazo-coupling reaction. II. Further evidence in favour of the polarisation theory. H. H. Hodgson and E. Marsden (*J. Soc. Dyers and Col.*, 1944, **60**, 16—19; cf. A., 1943, II, 8).—Examples are discussed of the decomp. of unstable equilibrium mixtures of diazonium and their isomeric diazo-compounds, whereby reactions of both types of compound could be simultaneously compared. Evidence is given supporting the theory developed previously (*loc. cit.*). A. T. P.

Separation of phenols and alkylated products thereof.—See B., 1944, II, 5.

Synthesis of 5-hydroxyindane. (Miss) K. Paranjape, N. L. Phalnikar, and K. S. Nargund (*J. Univ. Bombay*, 1943, **12**, **A**, Part 3, 66—67).—Addition of Et *cyclo*pentylideneacetate and HCO_2Et to Na in Et_2O at 0° and then at room temp. gives unstable Et 2-formyl-*cyclo*pentylideneacetate (*semicarbazone*, m.p. 201°), converted by $CH_2(CO_2H)_2$ in C_5H_5N containing a little piperidine at 100° followed by hydrolysis into cyclo*pentylideneacetic-2-β-acrylic acid*, m.p. 62°, in 80% yield. This is converted by heating at 150° with $Ba(OH)_2$ followed by distillation at 180°/80 mm. into 5-*keto*-$\Delta^{1:}$:"-*dihydroindane*, b.p. 105°/20 mm., 140°/80 mm. (*semicarbazone*, m.p. 161°), more conveniently obtained by condensation of 2-formyl*cyclo*pentanone with $COMe_2$ and NaOEt in EtOH. It is converted by long contact with fuming HCl in a sealed tube at room temp. into 5-hydroxyindane, m.p. 55° (benzoate, m.p. 106—107°). H. W.

Halogenated 2 : 2'-dihydroxydiphenylmethanes.—See B., 1944, II, 33.

Dienœstrol. G. I. Hobday and W. F. Short (*J.C.S.*, 1943, 609—612).—*α-Chloro-α-p-anisyl-*Δ^{α}*-propene*, m.p. 43°, is obtained from anetholc dichloride (**I**) and boiling EtOH–NaOEt, or from *p*-$OMe\cdot C_6H_4\cdot COEt$ (**II**) and PCl_5 at −5°, followed by aq. KOH–EtOH at room temp. *β-Chloro-α-p-anisyl-*Δ^{α}*-propene* (**III**), b.p. 135—136°/10 mm., is prepared from (**I**) and C_5H_5N at 100° (bath) or from anisylacetone and PCl_5. Crude (**III**) and boiling KOH–MeOH give *α-p-anisyl-*Δ^{α}*-propinene* (**IV**), b.p. 115—117°/9 mm. The structure of (**III**) is shown by ozonolysis in $CHCl_3$ to anisaldehyde (60%), and by the isolation of *β-p*-anisyl-α-methylacrylic acid (**V**) and a little *αδ-di-p*-anisyl-*βγ*-dimethyl-$\Delta^{\beta\gamma}$-butadiene, m.p. 162°, from the products of the successive action of Mg and CO_2 in Et_2O. Anethole dibromide (**VI**) and $NPhMe_2$ give *β-(N-methylanilino)anethole*, m.p. 116°; (**IV**) is also probably formed. *αβ*-Dibromo-*β-p*-anisyl*iso*butyric acid and dil. aq. NaOH afford *β-bromo-α-p-anisyl-*Δ^{α}*-propene* (**VII**), b.p. 130—132°/6 mm. (not the α-Br-derivative, as stated by Balaban *et al.*, B.P. 547,027; B., 1942, III, 246), also obtained from (**VI**) and boiling 1·7N-KOH–EtOH. (**VII**) gives a Grignard reagent, which when carbonated at −10° yields (**V**). (**VII**) and Mg give *αδ-di-p*-anisyl-*βγ*-dimethyl-$\Delta^{\beta\gamma}$-butadiene, m.p. 163° [ozonolysis products anisaldehyde (73%) and some Ac_2], reduced (H_2–Pd–C–$COMe_2$) to some *αδ-di-p-anisyl-βγ-dimethylbutane*, m.p. 68—69°; the latter is also obtained from *β*-chloro-*α-p*-anisylpropane and Mg in boiling Et_2O. *γδ-Di-p*-hydroxyphenylhexane-*γδ*-diol, m.p. 204—206°, gives a *dibenzoate*, m.p. 235—236°, and *di-p-toluenesulphonate*, m.p. 205°. *γδ-Di-p-anisylhexane-γδ-diol*, m.p. 194° [Ac_2O–AcCl give mainly *γγ-di-p*-anisylhexan-δ-one (see below)], is also obtained from (**II**)–$HgCl_2$–Et_2O–Mg–C_6H_6, or by electrolysis of (**II**) in aq. NaOH–EtOH, or from propionoin and SeO_2 (distil slowly), and treatment of the resulting dipropionyl with *p*-$OMe\cdot C_6H_4\cdot MgBr$. A second *form* (**VIII**) (*iso*pinacol), m.p. 94—95°, of *γδ-di-p*-hydroxyphenylhexane-*γδ*-diol is obtained as by-product on electrolytic reduction of *p*-$OH\cdot C_6H_4\cdot COEt$, or by electrolytic reduction of *p-benzoyloxypropiophenone*, m.p. 117°, in aq. NaOH–dioxan. Benzoylation of (**VIII**) yields probably its dibenzoate, readily converted into *γγ-di-p-benzoyloxyphenylhexan-δ-one*, m.p. 178°. (**VIII**) and warm AcOH or mineral acid give *γγ-di-p-hydroxyphenylhexan-δ-one*, m.p. 136°, which does not form CO-derivatives, but affords a diacetate, m.p. 91—92°, and a liquid Me_2 ether reducible by Na–$C_5H_{11}\cdot OH$ to stilbœstrol Me_2 ether; with KOH at 200°, it (or its diacetate) gives (probably) *αα-di-p*-hydroxyphenylpropane, m.p. 134° (Me_2 ether, m.p. 44°). (**IV**) and HBr–C_6H_6 at 0° (whence *α*-bromo-*α-p*-anisyl-Δ^{α}-propene; cf. Balaban, *loc. cit.*), followed by Mg and then $CuCl_2$, afford anethole, (?) (**IV**), and a resin; demethylation (MgMeI) of the last gives a little dienœstrol (**IX**), m.p. 230—233° [$(CH_2Ph)_2$ *ether*, m.p. 205°; *di-p-toluenesulphonate*, m.p. 168°; *dibenzoate*, m.p. 224°]. Some *Me_1 ether* (**X**), m.p. 142°, is obtained from (**IX**) and CH_2N_2 at room temp., whereas Me_2SO_4 (4 mols.) in N-NaOH yields (**X**) (73%) and the *Me_2 ether* (**XI**), m.p. 130—131°, also prepared [29% of (**X**) + 30% of (**XI**)] using MeI in boiling KOH–EtOH. Ozonolysis of (**XI**) in AcOH gives anisil (16%), converted into 2 : 3-*di-p-anisylquinoxaline*, m.p. 149—150°. (**X**) or (**XI**) is demethylated to (**IX**) by MgMeI, but gives an isomeride, iso*dienœstrol* (**XII**), m.p. 189°, with EtOH–KOH at 220°. (**XII**) is reduced (Pd–C) to a 2 : 1 mixture of hexœstrol and *iso*hexœstrol, and the liquid Me_2 ether of (**XII**) similarly yields (mainly) hexœstrol Me_2 ether. (**IX**) and (**XII**) are probably stereoisomerides. A. T. P.

Fluorescence of vitamin-*A*. H. Sobotka, (Miss) S. Kann, and E. Loewenstein (*J. Amer. Chem. Soc.*, 1943, **65**, 1959—1961).—The intensity of fluorescence of higher fatty acid esters of vitamin-*A* or its acetate in Et_2O, $CHCl_3$, or C_6H_6 rapidly decreases slightly but later only slowly; the "steady" val. is approx. ∝ concn. in the range 0·1—5·0 i.u. per ml. (cf. C., 1944, Part 1). In EtOH, however, there is a rapid great initial increase, followed by a slightly slower, but still rapid, decrease, finally to extinction. The highest val. obtained is increased by increasing the intensity of illumination. Cessation of illumination during the decrease gives after its resumption the same val. and the same rate of subsequent decline. The rate of decline is lowered by flushing with CO_2 or N_2. Vitamin-A_2 esters show the same phenomena, but cryst. -*A* itself shows only an immediate decline. Adding C_6H_6 to -*A* esters in MeOH, EtOH, or $Bu^{\beta}OH$ is without effect until with 65—70% of C_6H_6 a sudden complete change to the non-polar solvent behaviour occurs. R. S. C.

Conversion of lutein in a boric acid–naphthalene melt. I. L. Zechmeister and J. W. Sease (*J. Amer. Chem. Soc.*, 1943, **65**, 1951—1955).—Chromatography of lutein (prep. from *Tagetes* extract described) which has been heated at 140° in $C_{10}H_8$–H_3BO_3 yields *deoxylutein*-I (3—4%), m.p. 149° (corr.; in CO_2; block) [acetate, m.p. 139° (corr.)], -II (10%), m.p. 156·5—158° (corr.) after softening [acetate, softens 139°, m.p. 141° (corr.)], and -III (3—4%), m.p. 162° (corr.) after softening. All are $C_{40}H_{56}O$ ($\pm H_2$), have no vitamin-*A* activity (rats), contain 11 C:C and an esterifiable OH, resemble cryptoxanthin on partition, and undergo isomerisation by I, developing *cis*-peaks. Photomicrographs are given. -II and -III are brownish-orange, -I is redder. Absorption spectra of -II and -III are similar, showing several peaks, but -I shows only one peak (at 494 mμ.). Only 10 C:C are conjugated in -II and -III. Structural possibilities are discussed. R. S. C.

***cyclo*Alkanyl peroxides.**—See B., 1944, II, 34.

Chlorination product of benzyl thiocyanate. B. Holmberg (*Arkiv Kemi, Min., Geol.*, 1943, **16**, **B**, No. 12, 3 pp.).—Slow (2—3 hr.) chlorination of $CH_2Ph\cdot CNS$ in H_2O suspension at 0° gives *benzylsulphinyl cyanide* (**I**), m.p. 81—82°; $CH_2Ph\cdot SO_2H$ (**II**) (identified by reaction with $CH_2{:}CH\cdot CO_2H$ to $CH_2Ph\cdot SO_2\cdot[CH_2]_2\cdot CO_2H$) is formed in small amount only, by hydrolysis of (**I**) (cf. Johnson *et al.*, A., 1939, II, 498). (**I**) is rapidly hydrolysed to (**II**) by dil. NaOH. M. H. M. A.

Mercapturic acids. I. Synthesis of phenyl-*l*-cysteine and *l*-phenylmercapturic acid. S. H. Zbarsky and L. Young (*J. Biol. Chem.*, 1943, **151**, 211—215).—Treatment of *l*-cystine in 1·5N-H_2SO_4 at 100° with Zn dust with occasional additions of mossy Zn and of the filtrate with an aq. suspension of Cu_2O leads to cysteine Cu^{I} mercaptide, converted by $PhN_2\cdot HSO_4$ into phenyl-*l*-cysteine (**I**), decomp. 170—172°, $[\alpha]_D^{25}$ +11° in 0·1N-NaOH; (**I**) is also obtained by debromination (Na–Hg at room temp.) of *p*-bromophenyl-*l*-cysteine. *l*-Phenylmercapturic acid, m.p. 142°, $[\alpha]_D^{27}$ −23° in EtOH, is obtained by decomp. the product of the interaction of PhN_2Cl and acetylcysteine with Cu powder, by treatment of (**I**) with Ac_2O and N-NaOH at 0°, and by debromination of *p*-bromophenylmercapturic acid by Na–Hg. H. W.

Mechanism of chemical reactions. VII. Significance of molecular compounds in catalytic hydrogenations. III. Hydrogenation of mandelic acid and mandelic esters. K. Kindler and D. Kwok (*Annalen*, 1943, **554**, 9—15; cf. A., 1934, 879; 1935, 1362).—Catalytic hydrogenation (Pd sponge) of $OH\cdot CHPh\cdot CO_2H$ (**I**) in AcOH containing H_2SO_4 proceeds rapidly at room temp., giving $CH_2Ph\cdot CO_2H$ in 90% yield. In absence of H_2SO_4 hydrogenation occurs very slowly or not at all and ceases after absorption of ~15% of the theoretical quantity of the gas. The action is ascribed in part to the formation of mol. compounds $HX\cdot\cdot\cdot OH\cdot CHPh\cdot C(OH){:}O\cdot\cdot\cdot HX$ in which the asterisked atoms are so extensively saturated that the reductive removal of the greatly loosened alcoholic OH proceeds more readily than in (**I**), and in part to the production of esters $CHPhX\cdot CO_2H$ in which X is more readily removable than the OH of (**I**). $HClO_4$ has the same effect. Similarly $OH\cdot CHPh\cdot CO_2Et$ (**II**) is not hydrogenated in AcOH alone but in presence of H_2SO_4 or $HClO_4$ gives $CH_2Ph\cdot CO_2Et$ in ~85% yield. At 100°, (**II**) rapidly absorbs H_2 even in absence of H_2SO_4 or $HClO_4$; reaction ceases after absorption of 4 H_2 with production of Et *cyclo*hexylacetate (**III**); if the change is interrupted after absorption of 1 H_2 the products are $CH_2Ph\cdot CO_2Et$ (~90%) with traces of (**III**), the OH being reduced more rapidly than the ring. This difference in reactivity is much less when OAlk or Alk is substituted in the

nucleus. Thus Et *p*-ethylmandelate is converted by partial hydrogenation at 100° into a difficultly separable mixture of unchanged material, Et 4-ethyl*cyclo*hexylacetate, and a little *p*-$C_6H_4Et{\cdot}CH_2{\cdot}CO_2Et$. The rate of hydrogenation of (I) in presence of H_2SO_4 or $HClO_4$ diminishes with diminished concn. of mineral acid and also with increasing H_2O content of the mixture. $ZnCl_2$–HCl can replace H_2SO_4 or $HClO_4$. H. W.

High-pressure catalytic hydrogenation. I. Partial hydrogenation of diphenylacetic acid. A. Sandoval L. (*Ciencia*, 1943, **4**, 107—108).—$OAc{\cdot}CPh_2{\cdot}CO_2Me$ is hydrogenated (Raney Ni) to $CHPh_2{\cdot}CO_2Me$ and thence to Me *cyclo*hexylphenylacetate. F. R. G.

α-Chlorodiphenylacetic acid and its derivatives. S. A. Setlur, A. N. Kothare, and V. V. Nadkarny (*J. Univ. Bombay*, 1943, **12**, A, Part 3, 68—70).—$CPh_2Cl{\cdot}CO_2H$ (I) is converted by the requisite NaOAlk into *α-methoxy-*, m.p. 100°, and *α-ethoxy-*, m.p. 114°, *-diphenylacetic acid*. With $(NH_4)_2CO_3$ and conc. aq. NH_3 at 100° (I) gives a small proportion of *α-aminodiphenylacetic acid*, m.p. 245°, but much $OH{\cdot}CPh_2{\cdot}CO_2H$ is produced. With the respective amine in C_6H_6 at 100° (I) yields *α-benzylamino-*, m.p. 211° (decomp.), *α-o-toluidino-*, m.p. 150° (decomp.), *α-m-toluidino-*, m.p. 165° (decomp.), *α-m-nitroanilino-*, *α-o-carboxyanilino-*, m.p. 193° (decomp.), and *α-piperidino-*, m.p. 180° (decomp.), *-diphenylacetic acid*. Almost all the anilinodiphenylacetic acids are rapidly hydrolysed by conc. H_2SO_4, which gives a blood-red colour [as with (I)] on warming or keeping for some time. H. W.

Synthetic anthelmintics. VII, VIII. Compounds related to desmotroposantonin. (Miss) K. Paranjape, N. L. Phalnikar, and K. S. Nargund (*J. Univ. Bombay*, 1943, **12**, A, Part 3, 60—63).—VII. 1-Keto-7-methoxy-1 : 2 : 3 : 4-tetrahydronaphthalene (I), $CHMeBr{\cdot}CO_2Et$, and Zn turnings in boiling PhMe yield *Et α-1-hydroxy-7-methoxy-*1 : 2 : 3 : 4-*tetrahydro-*1-*naphthylpropionate*, b.p. 185°/25 mm., converted by P_2O_5 in C_6H_6 at 100° into *Et α-7-methoxy-*3 : 4-*dihydro-*1-*naphthylpropionate*, b.p. 175°/25 mm. The corresponding *acid*, b.p. 215°/25 mm., is transformed by the protracted action of 60% H_2SO_4 at room temp. into *α-2-hydroxy-7-methoxy-*1 : 2 : 3 : 4-*tetrahydro-*1-*naphthylpropionolactone*, b.p. 210°/25 mm., demethylated (HBr in AcOH) to *α-2 : 7-dihydroxy-*1 : 2 : 3 : 4-*tetrahydro-*1-*naphthylpropionolactone*, b.p. 240°/25 mm.

VIII. (I), $Me_2C_2O_4$, and MeOH–NaOMe give *Me* 1-*keto-7-methoxy-*1 : 2 : 3 : 4-*tetrahydro-*2-*naphthylglyoxylate*, m.p. 57° (semicarbazone, m.p. 225°), which at 150—180° followed by distillation affords *Me* 1-*keto-7-methoxy-*1 : 2 : 3 : 4-*tetrahydronaphthalene-*2-*carboxylate*, b.p. 205°/70 mm., m.p. 57·5° (violet colour with $FeCl_3$). This with Na and $CH_2Br{\cdot}CO_2Et$ gives *Et* 1-*keto-*2-*carbomethoxy-7-methoxy-*1 : 2 : 3 : 4-*tetrahydro-*2-*naphthylacetate*, m.p. 61°, which could not be hydrolysed under any conditions. (I) and Br in CS_2 afford 2-*bromo-*1-*keto-7-methoxy-*1 : 2 : 3 : 4-*tetrahydronaphthalene* (II), m.p. 48°. (I) is converted by successive treatments with $NaNH_2$ in boiling Et_2O and $CH_2Br{\cdot}CO_2Et$ followed by hydrolysis into 1-*keto-7-methoxy-*1 : 2 : 3 : 4-*tetrahydro-*2-*naphthylacetic acid* (III), m.p. 88°. (II) and $CHNa(CO_2Et)_2$ in boiling C_6H_6 afford Et_2 1-keto-7-methoxy-1 : 2 : 3 : 4-tetrahydro-2-naphthylmalonate, which on acid hydrolysis yields (III) and is reduced by $Al(OPr^{\beta})_3$ in boiling $Pr^{\beta}OH$ and then hydrolysed to 1-*hydroxy-7-methoxy-*1 : 2 : 3 : 4-*tetrahydro-*2-*naphthylacetic acid*, m.p. 88°; this is converted at 100° into the corresponding *lactone*, m.p. 76°, demethylated to 1 : 7-*dihydroxy-*1 : 2 : 3 : 4-*tetrahydro-*2-*naphthylacetolactone*, m.p. 101°. (II) and $CMeNa(CO_2Et)_2$ in C_6H_6 afford Et_2 1-keto-7-methoxy-1 : 2 : 3 : 4-tetrahydro-2-naphthylmethylmalonate, which gives *α-1-keto-*, m.p. 91°, and *α-1-hydroxy-7-methoxy-*1 : 2 : 3 : 4-*tetrahydro-*2-*naphthylpropionic acid*, m.p. 77°; the corresponding *lactone*, m.p. 83°, is demethylated to *α-*1 : 7-*dihydroxy-*1 : 2 : 3 : 4-*tetrahydro-*2-*naphthylpropionolactone*, m.p. 112°. H. W.

Electrolytic reduction of *p*-nitro- to *p*-amino-benzoic acid. P. H. Ravenscroft, R. W. Lewis, and O. W. Brown (*Trans. Electrochem. Soc.*, 1943, **84**, *Preprint* 2, 11—17).—*p*-$NO_2{\cdot}C_6H_4{\cdot}CO_2H$ (I) is reduced to *p*-$NH_2{\cdot}C_6H_4{\cdot}CO_2H$ (II) in yields of 98—98·5% using, *e.g.*, a Sn cathode, a catholyte consisting of 500 c.c. of 14·1 wt.-% HCl, 5 g. of (I), 3—5 g. of $SnCl_2,2H_2O$, and a c.d. of 8 amp. per sq. dm. at 70°. Temp., acid concn., and c.d. must be controlled so that $Sn^{\cdot\cdot}$ ions remain in solution until sufficient current to reduce (I) has passed. With a Pb cathode at 70°, a c.d. of 6 amp. per sq. dm., a catholyte consisting of 500 c.c. of 8·7 wt.-% HCl, and 5 g. of (I) 94—95% yields of (II) were obtained. (II) was separated by neutralisation of its hydrochloride with NaOH to the isoelectric point. H. Sch.

Electrolytic reduction of aromatic trinitro-compounds to triamines by use of a carrier catalyst. R. W. Lewis and O. W. Brown (*Trans. Electrochem. Soc.*, 1943, **84**, *Preprint* 1, 1—9).—A $SnCl_2$ carrier-catalyst was employed in the electrolytic reduction of 1 : 2 : 4 : 6-$C_6H_3R(NO_2)_3$ (I) (R = CO_2H, OH, Me) to the $C_6H_3R(NH_2)_3$ (II). The method has several advantages over the method using a Pb cathode. The best conditions for complete reduction to (II) are: a Sn cathode, a catholyte (total vol. 500 c.c.) of 1 : 1 (vol.) HCl containing respectively 3·95, 4·43, or 4·47 g. of $SnCl_2,2H_2O$, and (usually) 5 g. of (I), a c.d. of 7—8 amp. per sq. dm., and a temp. of 35°. Yields and current efficiencies under these conditions are 93—97%. To obtain high yields of (II) temp., acid concn. of the catholyte, and c.d. must be controlled so that the $Sn^{\cdot\cdot}$ ions remain in solution until sufficient current to reduce (I) has passed. The $Sn^{\cdot\cdot}$ ions are mainly responsible for the reduction. H. Sch.

Electrolytic reduction of cinnamic acid. New preparative method for *βγ*-diphenyladipic acid. C. L. Wilson and K. B. Wilson (*Trans. Electrochem. Soc.*, 1943, **84**, *Preprint* 4, 25—35; cf. B., 1943, II, 276).—Reduction of $CHPh{:}CH{\cdot}CO_2H$ (I) at a Hg cathode in aq. H_2SO_4 in presence of a H_2O-sol. org. solvent (*e.g.*, EtOH) gives <10% of $Ph{\cdot}[CH_2]_2{\cdot}CO_2H$, ~45% (55% under most favourable conditions) of a ~1 : 1 mixture of *meso-* (II) (*Me* ester, m.p. 166—168°) and *dl-* (III) $-(CHPh{\cdot}CH_2{\cdot}CO_2H)_2$, and ~45% of a partly reduced polymer (IV) which seems to be formed by union of 2 or more mols. of (I) with reduction of some of the CO_2H groups. The yield of (II) + (III) is not materially altered when (I) is replaced by its Et ester, and is highest when $OH{\cdot}[CH_2]_2{\cdot}OEt$ and $NMe_2{\cdot}CHO$ are added to the catholyte. (IV), readily separated by its solubility in cold C_6H_6, is a viscous liquid, equiv. ~300 [*i.e.*, 1 CO_2H to 2 mols. of (I)]. With 85% H_2SO_4 at 100°, (II) and (III) give the known *trans-* and *cis-*diketohexahydrochrysene, respectively. Similar reduction of *o*-$C_6H_4Cl{\cdot}CH{:}CH{\cdot}CO_2H$ gives *βγ-di-o-chlorophenyladipic acid*, forms, m.p. 301—307° and 197—200°. *p*-$OMe{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CO_2H$ affords *dianisyladipic acids*, m.p. 257—258° and 178—180°. Reduction of *o*-$CN{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CO_2H$ in presence of 30% H_2SO_4 gives (probably) *di(cyanophenyl)adipic acid*, m.p. 310—314° (decomp.), and (probably) *β-o-carbamylphenylpropionic acid* (V), m.p. 173—174°. In 25% H_2SO_4 only (V), m.p. 176—178°, is formed. 10% NaOH converts (V) at 100° into *β-o*-carboxyphenylpropionic acid. The viscous reduction product of *m*-$OH{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CO_2H$ gives after methylation mixed di-*m*-anisyladipic acids (form, m.p. 247—250°, isolable). H. Sch.

Addition of maleic anhydrides to substituted styrenes. M. Lora Tamayo (*Anal. fís. quím.*, 1943, **39**, 209—214).—Differences between the adduct of $(CH{\cdot}CO)_2O$ and anethole previously obtained (A., 1941, II, 134) and that of Hudson and Robinson (A., 1942, II, 53) are attributed to differences in experimental conditions. F. R. G.

Condensation of *n*-alkylsuccinic anhydrides with anisole. S. U. Mehta, K. V. Bokil, and K. S. Nargund (*J. Univ. Bombay*, 1943, **12**, A, Part 3, 64—65).—Anhyd. $AlCl_3$ is added gradually to a mixture of the *n*-alkylsuccinic anhydride and PhOMe in $PhNO_2$ at >40°; after 4 hr. at room temp. the mixture is decomposed with ice and HCl. Thus are obtained: *α-p*-methoxyphenacyl-propionic acid, m.p. 141° (*Me*, b.p. 173—180°/18 mm., and *Et*, b.p. 190°/30 mm., ester), *-butyric acid*, m.p. 108—109° (*semicarbazone*, m.p. 155°; *Me* ester, m.p. 56—57°), *-valeric acid*, m.p. 88—89° (*semicarbazone*, m.p. 145°), *-heptoic acid*, m.p. 80° (*semicarbazone*, m.p. 135°; *Me* ester, m.p. 41—42°), *-octoic acid*, m.p. 92° (*semicarbazone*, m.p. 142°), *-hexadecoic acid*, m.p. 99—100° (does not form a semicarbazone; *Me* ester, m.p. 45°), and *-octadecoic acid*, m.p. 85—86° (*semicarbazone*, m.p. 170—171°; *Me*, m.p. 38—39°, and *Et*, m.p. 41—42°, ester). H. W.

Preparation of derivatives of 2 : 2-dialkyl*cyclo*hexanone. A. J. Birch (*J.C.S.*, 1943, 661—662; cf. Johnson, A., 1943, II, 330).—2-Methyl*cyclo*hexanone, piperonal (I), and EtOH–NaOEt at room temp. for 4 days afford 6-*piperonylidene-*2-*methyl*cyclo*hexanone*, m.p. 74—75°, converted by $NaNH_2$ in boiling PhMe, followed by MeI, into 6-*piperonylidene-*2 : 2-*dimethyl*cyclo*hexanone*, m.p. 67° [also obtained from 2 : 2-dimethyl*cyclo*hexanone and $NaNH_2$ in boiling C_6H_6 followed by (I)], or by $NaNH_2$–C_6H_6, then EtI, into 6-*piperonylidene-*2-*methyl-*2-*ethyl*cyclo*hexanone*, m.p. 60—61°. A. T. P.

Condensation of ethylene oxide with cyclic β-keto-esters.—See A., 1944, II, 70.

Ionone. I. Cleavage of ethyl ionylideneacetate. H. Sobotka, (Miss) E. Bloch, and D. Glick (*J. Amer. Chem. Soc.*, 1943, **65**, 1961—1963).—*α-* and *β*-Ionone give, by the method of Karrer *et al.* (A., 1932, 852; 1933, 605), probably the same Et ionylideneacetate, b.p. 155°/1 mm., which, by distillation of the derived Ba salt with $(HCO_2)_2Ba$ and SiO_2 or soft glass at 150°/2 mm., gives *α*-ionone (2 : 4-dinitrophenyl-, m.p. 143°, and *p*-chlorobenzoyl-hydrazone, m.p. 214—215°; phenylsemicarbazone, m.p. 183—184°) (cf. Heilbron *et al.*, A., 1935, 978; 1936, 983). *β*-Ionone-2 : 4-dinitrophenyl-, m.p. 125—127°, and *-p*-chlorobenzoyl-hydrazone, m.p. 218—219°, and -phenylsemicarbazone, m.p. 160—162°, are described. R. S. C.

Electrolytic production of benzoquinone and quinol.—See B., 1944,

IV.—STEROLS AND STEROID SAPOGENINS.

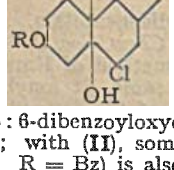
Water-soluble derivatives of vitamin-*D*.—See B., 1944, III, 19.

Minor sterols of yeast. XII. Hydrogenation of sterols. H. Wieland and W. Benend [with, in part, F. Rath] (*Annalen*, 1943, **554**, 1—8).—Further evidence is adduced in favour of the view that

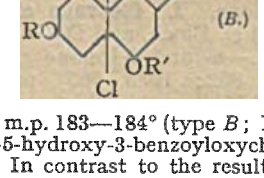
catalytic hydrogenation of poly-unsaturated sterols occurs in such a manner that the saturation of reactive double linkings is accompanied by a displacement of the inert double linking also present. This retains its passive character and is displaced from $\Delta^{7:8}$, $\Delta^{8:9}$, or $\Delta^{9:11}$ to $\Delta^{8:14}$. *iso*Dehydrocholesterol is hydrogenated (Pt in AcOH) to α-cholestenol, m.p. 119—120° (acetate, m.p. 77—78°), also obtained in presence of Pd–C in EtOAc, whereas with Pt in EtOAc the product is δ-cholestenol, m.p. 120°, $[\alpha]_D^{20}$ +11° (acetate, m.p. 107—108°, $[\alpha]_D^{20}$ +12·5°). 7-Dehydrocholesteryl benzoate is hydrogenated (Pt in EtOAc) to γ-cholestenyl benzoate, m.p. 157°, clear at 176°. Ergosteryl benzoate (**I**) is hydrogenated (PtO_2 in EtOAc) to γ-ergostenyl benzoate (**II**), m.p. 179°, $[\alpha]_D^0$ ±0°, hydrolysed (KOH–MeOH) to γ-ergostenol (**III**), m.p. 148°, $[\alpha]_D^{20}$ ±0° [acetate, m.p. 160°, also obtained (m.p. 158°) by hydrogenation (Pt in EtOAc) of γ-ergosteryl acetate]; under somewhat different conditions (**I**) is converted (PtO_2 in EtOAc) into γ-dihydroergosteryl benzoate (**IV**), m.p. 193—195°, $[\alpha]_D^{20}$ −8° in $CHCl_3$, hydrolysed to γ-dihydroergosterol (**V**), m.p. 173—175°, $[\alpha]_D^{20}$ −21° in $CHCl_3$ (acetate, m.p. 180—181°, $[\alpha]_D$ −21° in $CHCl_3$. (**V**) is hydrogenated (Pt in EtOAc) to (**III**), m.p. 145—146°, also obtained by use of Na·in EtOH; similarly (**IV**) is hydrogenated to (**II**). The transition of ascosterol into fæcosterol appears exceptional. H. W.

Sterol group. XLV. Investigation of the homogeneity of sitosterol by oxidation with the Oppenauer reagent. D. H. R. Barton and E. R. H. Jones (*J.C.S.*, 1943, 599—602; cf. A., 1942, II, 286).—Oppenauer oxidation, followed by chromatographic analysis of the ketones, is of great val. for examining the homogeneity of sitosterols, and in particular for determining the approx. proportion of sitostanol. It provides a convenient criterion of purity and may be generally applicable in the steroid series. Tall-öl sitosterol (**I**), m.p. 137—138°, after oxidation (Oppenauer) and chromatographic analysis (large columns; adsorbent : adsorbate : : 100 : 1) thus affords 66% of sitostenones, mainly Δ^4-β-sitostenone (**II**), new m.p. 88° [oxime, m.p. 175·5°; semicarbazone, m.p. 250° (decomp.); 2 : 4-dinitrophenylhydrazone, m.p. 253° (decomp.)], and a little of a closely-related sitostenone, m.p. 86°; 3·2% of unidentified ketone (**III**) (mainly αβ-unsaturated), m.p. ~115°, and 3·8% of unoxidised (**I**) are also isolated. Similar treatment of sitosterol (**IV**), m.p. 137—138°, from wheat-germ oil gives sitostenones (69·5%) [mainly (**II**)], triacontane (0·3%) [also isolable from (**IV**)], (**III**) (1·8%), and recovered (**IV**) (1·5%). The small amount of sitostanol present in (**I**) and (**IV**) is oxidised to sitostanone, m.p. 157° [2 : 4-*dinitrophenylhydrazone*, m.p. 223° (decomp.)] [2·5% or 5·9% from (**I**) or (**IV**), respectively]. A. T. P.

β-Cholesterol oxide. R. A. Baxter and F. S. Spring (*J.C.S.*, 1943, 613—615).—Oxidation [BzO_2H or o-$CO_2H{\cdot}C_6H_4{\cdot}CO_3H$ (cf. Chakravorty *et al.*, A., 1943, II, 58)] of cholesteryl benzoate gives a mixture of the α-benzoate oxide, m.p. 168—169°, and "αβ-cholesteryl benzoate oxide" (**I**), m.p. 150—151°, $[\alpha]_D^0$ +3·6° (all vals. in $CHCl_3$) (previously described as the β-derivative; A., 1939, II, 477). (**I**) is hydrolysed to "αβ-cholesterol oxide" (**II**), m.p. 107—108°, $[\alpha]_D^1$ −15° (previously described by many investigators as the β-oxide), and the suggestion of Hattori (*J. Pharm. Soc. Japan*, 1940, **60**, 334) that it is a 1 : 1 mixed crystal of α-cholesterol oxide (**III**) and β-cholesterol oxide (**IV**) is confirmed; (**IV**), m.p. 131—132°, $[\alpha]_D^{18\cdot5}$ +11·5° [acetate (**V**), m.p. 111°, $[\alpha]_D^{18}$ ±0°; *benzoate* (**VI**), m.p. 172—173°, $[\alpha]_D^{22}$ +16°], identical with the (**IV**), m.p. 136°, of Hattori, is isolated from the mother-liquors of (**II**). (**II**) can be prepared from equal parts of (**III**) and (**IV**) in MeOH. Vals. of $[\alpha]$ indicate that (**I**) is a 1 : 2 mixed crystal of the α-benzoate oxide and (**VI**). Fission of (**III**) and its derivatives with HCl affords solely chlorohydrins of type *A*. Fission of (**II**) and its derivatives is more complicated. (**II**) or (**I**) and BzCl–C_5H_5N at 100° (bath) give



(*A*.)



(*B*.)

5-chloro-3 : 6-dibenzoyloxycholestane, m.p. 183—184° (type *B*; R = R′ = Bz); with (**II**), some 6-chloro-5-hydroxy-3-benzoyloxycholestane (*A*; R = Bz) is also formed. In contrast to the results of Chakravorty *et al.* (*loc. cit.*), αβ-cholesteryl acetate oxide (**VII**) affords 5-*chloro*-6-*benzoyloxy*-3-*acetoxycholestane* (**VIII**), m.p. 176°, $[\alpha]_D^{22}$ −75·8°, and a little 6-chloro-5-hydroxy-3-acetoxycholestane (**IX**), m.p. 186—187°. (**VII**) and HCl in $CHCl_3$ affords 5-chloro-6-hydroxy-3-acetoxycholestane (**X**), new m.p. 190—191° (cf. Hattori) (*B*: R = Ac, R′ = H), and (**IX**), whereas interaction with HCl–EtOH gives 5-chloro-3 : 6-dihydroxycholestane, m.p. 171°, $[\alpha]_D^{19}$ −22·5° (*B*; R = R′ = H), the latter being formed also from (**II**) and HCl in $CHCl_3$ or EtOH. Fission of (**IV**) and its derivatives affords chlorohydrins of type *B* in ~90% yield. With BzCl–C_5H_5N, (**VI**) gives 5-chloro-3 : 6-dibenzoylcholestane, and (**V**) yields (**VIII**). With HCl in $CHCl_3$, (**V**) gives (**X**). A. T. P.

Œstradiol derivatives.—See B., 1944, III, 17.

Steroid ketones.—See B., 1944, III, 17, 18.

Sterol group. XLVI. Isolation of a new form of Δ^4-cholestenone. D. H. R. Barton and E. R. H. Jones (*J.C.S.*, 1943, 602—603; cf., A., 1942, II, 286).—Oppenauer oxidation of cholesterol and careful chromatographic analysis of the product gives Δ^4-cholestenone in two interconvertible forms, m.p. 88° and 82°, both $[\alpha]_D$ +92·2° in $CHCl_3$ (cf. lit.), which afford the same semicarbazone and 2 : 4-dinitrophenylhydrazone. Vals. of $[\alpha]$ and light-absorption intensities of both forms are slightly > those previously recorded. A. T. P.

VI.—HETEROCYCLIC.

Derivatives of furfuraldehyde; determination of their physicochemical constants. H. Paillard and R. Szasz (*Helv. Chim. Acta*, 1943, **26**, 1856—1861).—Appreciable amounts of tetrahydrofurfuraldehyde (**I**) are not obtained from tetrahydrofurfuryl alcohol (**II**) by catalytic dehydrogenation (Bouveault) at 270—450°, by oxidation by air in xylene containing quinoline, m-$C_6H_4(NO_2)_2$, or finely-divided Cu, by SeO_2 or N_2O_4, by CrO_3, by O_3, or by electrolytic oxidation. Treatment of tetrahydrofurfuryl chloride, b.p. 149—150°/720 mm., with $Pb(NO_3)_2$ or hydrolysis of tetrahydrofurfurylidene chloride does not afford (**I**). (**II**) is converted by Na and the requisite alkyl halide into *tetrahydrofurfuryl* iso*butyl*, b.p. 65—67°/8 mm., n-*amyl*, b.p. 89—91°/12 mm., n-*heptyl*, b.p. 122—124°/12 mm., n-*octyl*, b.p. 139—142°/12 mm., *phenyl*-n-*propyl*, b.p. 165—167°/12 mm., and *cinnamyl*, b.p. 182—183°/13 mm., *ether*. (**II**), Na, and PrβBr afford propylene whilst resins are derived from NaOPrβ and tetrahydrofurfuryl bromide. *d*, *n*, surface tension, parachor, and dielectric const. are recorded for the ethers. H. W.

Condensation of phenols with αβ-unsaturated aldehydes. E. Adler and S. Tingstam (*Arkiv Kemi, Min., Geol.*, 1943, **16**, **B**, No. 18, 7 pp.).—Addition of CH_2:CH·CHO (1 mol.) slowly (15 hr.) to o-4-xylenol (**I**) in glacial AcOH at 5° in presence of a trace of HCl yields an alkali-insol. compound, m.p. 185° (not investigated further), and 1-(2′ : 4′-*dimethylphenoxy*)-2 : 4 : 6-*trimethyl*-1 : 2-*dihydrobenzfuran* (**II**), m.p. 89°. The constitution of (**II**) follows from its insolubility in alkali, stability to Ac_2O–C_5H_5N, Br, and $KMnO_4$, and its conversion on Zn-dust distillation into (**I**) and 2 : 4 : 6-trimethylbenzfuran (**III**). (**II**) with hot conc. HBr–AcOH yields (**I**), much resin, and traces of (probably) (**III**). M. H. M. A.

Synthesis of cantharidin. (Miss) K. Paranjape, N. L. Phalnikar, B. V. Bhide, and K. S. Nargund (*Current Sci.*, 1943, **12**, 256—257).—$CMeAcNa{\cdot}CO_2Et$ and I afford Et_2 αα′-diacetyl-αα′-dimethylsuccinate, which is brominated and then converted by mol. Ag into Et_3 3 : 6-diketo-1 : 2-dimethyl*cyclo*hexane-1 : 2-dicarboxylate (**I**). Clemmensen reduction of (**I**) followed by hydrolysis affords deoxycantharidin. Reduction of (**I**) by $Al(OPr^{\beta})_3$ followed by etherification and hydrolysis by H_2SO_4 yields cantharidin, m.p. 217°, identical with a sample obtained from *Mylabris pustulata* (cf. Woodward *et al.*, A., 1942, II, 142). No experimental details are given. H. W.

Steric isomerides of α-tocopherol. P. Karrer and H. Rentschler (*Helv. Chim. Acta*, 1943, **26**, 1750—1758).—(−)-Phytyl bromide and trimethylquinol (**I**) afford [$C_{(2)}$-dl, $C^*_{(\delta)}C^*_{(\theta)}$-l]-α-*tocopherol* (**II**), which is sterically homogeneous at $C_{(\delta)}$ and possibly at $C_{(\theta)}$ but racemic at $C_{(2)}$. It gives an *allophanate*, m.p. 192°, and a non-cryst. *acetate*. Attempted resolution of (**II**) by means of 3-bromo-*d*-camphor-7′-sulphonyl chloride does not give decisive results. The compound obtained from (**I**) and natural *d*-phytol is possibly optically homogeneous with respect to $C_{(\delta)}$ and $C_{(\theta)}$ and racemic with respect to $C_{(2)}$, and hence is designated [$C^*_{(2)}dl$, $C^*_{(\delta)}C^*_{(\theta)}$-*d*]-α-tocopherol. (**II**) and the product from (**I**) and synthetic *dl*-phytol is racemic with respect to all three asymmetric C and hence is termed [$C^*_{(2)}dl$, $C^*_{(\delta)}C^*_{(\theta)}$-*dl*]-α-tocopherol (**III**). Optical activity cannot be detected in (**I**) and (**II**) or its acetate and no differences are observed in the m.p. of the allophanates, dinitrobenzoates, and p-nitrophenylurethanes of (**I**), (**II**), and (**III**). The physiological activities of (**I**), (**II**), (**III**), and natural α-tocopherol (**IV**) are identical within the limits of experimental error. The sole marked difference between the physical properties of (**IV**) and (**I**), (**II**), and (**III**) is the m.p. of the allophanate (161—162° and 172—173° respectively). Reply is made to John (A., 1942, II, 421). H. W.

Halogenated 1 : 3-dioxans.—See B., 1944, II, 6.

Dioxan derivatives.—See B., 1944, II, 35.

Ethyl 4-phenyl-1-methylpiperidine-4-carboxylate.—See B., 1944, II, 35.

2 : 4-Diarylpyrroles. I. Synthesis of 2 : 4-diarylpyrroles and 2 : 2′ : 4 : 4′-tetra-arylazadipyrromethines. II. Methines. III. 3-Amino-2 : 4-diphenylpyrrole. M. A. T. Rogers (*J.C.S.*, 1943, 590—596, 596—597, 598—599).—I. γ-Nitro-β-phenylbutyrophenone with HCO_2NH_4 at 180—190° gives some 2 : 4-*diphenylpyrrole* (**I**), m.p. 178—179°, and 2 : 2′ : 4 : 4′-*tetraphenylazadipyrromethine* (**II**), m.p. 287—288°, a deep blue substance containing a new chromo-

phoric system. Compounds similarly prepared are: 2 : 2′-*diphenyl*-4 : 4′-*di*-(m-*nitrophenyl*)-, m.p. 330°, from *γ-nitro-β*-(m-*nitrophenyl*)-*butyrophenone*, m.p. 74—77°; -(m-*hydroxyphenyl*)-, m.p. 304—306°, from *γ-nitro-β*-(m-*hydroxyphenyl*)*butyrophenone*, m.p. 96—98°; -(p-*dimethylaminophenyl*)-, m.p. 276—278° (*dimethiodide*), from *γ-nitro-β*-(p-*dimethylaminophenyl*)*butyrophenone*, m.p. 114—115° (*oxime*, m.p. 121—123°); -(3 : 4-*methylenedioxyphenyl*)-, m.p. 258—259°; and -(p-*acetamidophenyl*)-, m.p. ~370°, from *β-benzoyl-α*-(p-*acetamidophenyl*)*propionitrile*, m.p. 163—164·5°; 4 : 4′-*diphenyl*-2 : 2′-*di*-p-*anisyl*-, m.p. 239—242°, from *γ-nitro-β*-*phenyl*-p-*methoxybutyrophenone*, m.p. 92—93°; 2 : 2′-*diphenyl*-4 : 4′-*di*-p-*anisyl*-, m.p. 288—290°, from *γ-nitro-β*-p-*anisylbutyrophenone*, m.p. 66°; and 2 : 2′ : 4 : 4′-*tetra*-p-*anisyl-azapyrromethine*, m.p. 281—282°. Metal complexes of certain of the compounds are described, *e.g.*, *Cu*, *Co*, *Ni*, and *Zn bis*-(2 : 2′ : 4 : 4′-*tetraphenylazadipyrromethine*). Se-dehydrogenation of 2 : 4-diphenylpyrrolidine affords (I). Reduction (H_2–Ni) of *β-p*-anisoyl-α-phenylpropionitrile yields 4-*phenyl*-2-p-*anisyl-pyrroline*, b.p. 235—250°, m.p. 74—75° (*picrate*, m.p. 180—181°), dehydrogenated (Se) to the *-pyrrole*, m.p. 205—207°. 2-*Phenyl*-4-p-*anisyl-pyrroline*, b.p. 232—238°/7 mm., s.p. 27° (*picrate*, m.p. 156—158°), and *-pyrrole* (**III**), m.p. 197—199°, are similarly obtained. Nitrosation (HCl–$NaNO_2$) of (I) leads to 5-*nitroso*-2 : 4-*diphenylpyrrole* (**IV**), m.p. 139—140° [*hydrochloride*, m.p. 190° (decomp.); *picrate*, m.p. 188° (decomp.)], which is reduced (H_2–PtO_2) to the 5-NH_2-compound, m.p. 155—156° (*Ac* derivative, m.p. 171—172°). 5-*Nitroso*-2-*phenyl*-4-p-*anisyl*- (**V**) [*base*, m.p. 176—177° (decomp.)], and -4-*phenyl*-2-p-*anisyl*-*pyrrole hydrochloride* (+MeOH), decomp. 170°, are similarly prepared. Condensation of (I) and (**IV**) in AcOH–Ac_2O leads to (**II**), and 2 : 2′ : 4-*triphenyl*-4′-p-*anisylazadipyrromethine*, m.p. 256—257°, is obtained from (**IV**) and (**III**) or (I) and (V). Degradation of (**II**) by 55% HI gives (I); the solution of (**II**) in moist dioxan, C_5H_5N, or OH·$[CH_2]_2$·OEt is reduced by $NaHSO_3$ to a nearly colourless leuco-compound, readily reoxidised to (**II**) by air. *γ-Nitro-β-phenyl-hexophenone*, m.p. 156—158°, and *-butyrophenoneoxime*, m.p. 108—110°, are also described.

II. CH(OEt)$_3$ and (I) in AcOH give 2 : 2′ : 4 : 4′-*tetraphenyldipyrromethine* (**VI**), m.p. 284—286° (*Cu bis*-complex, 2 methine = 1 Cu). HCO·NPhMe, $POCl_3$, and (I) yield 2 : 4-*diphenylpyrrole*-5-*aldehyde*, m.p. 187—188° [*oxime*, m.p. 202° (slow decomp.); p-*nitrophenylhydrazone*, m.p. 241—242°], which gives α-(2 : 4-*dinitrophenyl*)-*β*-(2 : 4-*diphenyl*-5-*pyrrolyl*)*ethylene*, m.p. 254—255°, with 1 : 2 : 4-$C_6H_3Me(NO_2)_2$]; condensed with (I) it affords (**VI**) and is reduced (Ni–H_2) to the *-carbinol*, m.p. ~170° (decomp.). 2-*Phenyl*-4-p-*anisylpyrrole*-5-*aldehyde*, m.p. 158—159° (*oxime*, m.p. 196—198°, mixture of *syn*- and *anti*-forms), similarly prepared, with (**III**) yields 2 : 2′ : 4-*triphenyl*-4′-p-*anisyldipyrromethine*, m.p. 240—247°. $CPhCl_3$ and (I) in AcOH give 2 : 2′ : 4 : 4′-*tetraphenyl*-meso-*phenyldipyrromethine*, m.p. 268—270°, the *Cu* complex of which contains 1 methine = 1 Cu.

III. The blue compound obtained by Gabriel (cf. A., 1908, i, 464) from 3-amino-2 : 4-diphenylpyrrole (**VII**) and PhCHO in air is shown to be 3 : 3′-*dibenzylideneamino*-2 : 2′ : 4 : 4′-*tetraphenyl*-meso-*phenyldipyrromethine*. Benzoylation of (**VII**) affords the 3-NHBz-compound (**VIII**) and a red compound, 3 : 3′-*dibenzamido*-2 : 2′ : 4 : 4′-*tetraphenyl*-meso-*phenyldipyrromethine*, m.p. 345° (decomp.), also obtained from (**VIII**) and $CPhCl_3$. F. R. S.

2-Halogeno-5-sulphanilamidopyridines.—See B., 1944, III, 18.

Pyridine derivatives.—See B., 1943, III; 303; 1944, II, 6.

Nitration of isatin. W. C. Sumpier and W. F. Jones (*J. Amer. Chem. Soc.*, 1943, **65**, 1802—1803).—By the methods of Baeyer (A., 1879, 938), Rupe *et al.* (A., 1924, i, 764), or Calvery *et al.* (A., 1926, 187), isatin gives the 5-NO_2-derivative (85%), m.p. 254—255° [phenylhydrazone, m.p. 295° (lit., 284°, 286°)], the structure of which is proved by oxidation by H_2O_2–NaOH–H_2O to 5 : 2 : 1-NO_2·$C_6H_3(NH_2)$·CO_2H (86%), m.p. 278° (decomp.) (Ac derivative, m.p. 221°) (cf. Rupe *et al.*, A., 1926, 843). R. S. C.

Benzoylated derivatives of indigotin. VII. H. de Diesbach, G. Rey-Bellet, and T. S. Klang (*Helv. Chim. Acta*, 1943, **26**, 1869—1885).—2-*o*-Carboxyphenylquinoline-4-carboxylic acid is reduced (Na–Hg) in alkaline solution to the *lactam* (I), m.p. 239°, of 2-*o*-carboxyphenyl-1 : 2 : 3 : 4-tetrahydroquinoline-4-carboxylic acid (*Me* ester, m.p. 175°), decarboxylated to 2-*o*-*carboxyphenyl*-1 : 2 : 3 : 4-*tetrahydroquinoline*, m.p. 140°, and oxidised by CrO_3 in AcOH to the *lactam* (**II**), m.p. 168°, of 4-keto-2-*o*-carboxyphenyl-1 : 2 : 3 : 4-tetrahydroquinoline (*phenylhydrazone*, m.p. 222°; *CHPh* derivative, m.p. 228°; unstable 3-*Br*-compound, m.p. 257°). This is converted into the *lactam* (**III**), m.p. 267°, of 4-keto-2-*o*-carboxyphenyl-1 : 4-dihydroquinoline by heating with Se, SeO_2, or S, by treatment with PCl_5, and by bromination in $CHCl_3$ followed by removal of a mol. of HBr by boiling with C_5H_5N. This compound is not identical with that obtained by Hope *et al.* (A., 1933, 1060) by degradation of Höchst-yellow R, thus disproving the constitution assigned to this dye and also to Hochst-yellow U. Alternatively (**III**) is obtained by condensing *o*-NH_2·C_6H_4·COMe with *o*-$C_6H_4(CO)_2O$ to *o-phthaloylamidoacetophenone*, m.p. 135°, which is heated with P_2O_5 at 160°. (**III**) is transformed by alkali into 4-*keto*-2-*o*-*carboxyphenyl*-1 : 4-*dihydroquinoline*, m.p. 263° (recyclisation) (*Me* ester, m.p. 314°). (**III**) is converted by Br in boiling $CHCl_3$ into a *perbromide*, also formed in AcOH, in which it passes on prolonged treatment into the *lactam*, m.p. 233°, of 3-bromo-4-keto-2-*o*-carboxyphenyl-1 : 4-dihydroquinoline. (**III**) is converted by P_2S_5 in boiling C_6H_6 into the *lactam*, m.p. 253—254°, of 4-thio-2-*o*-carboxyphenyl-1 : 4-dihydroquinoline, which with excess of NHPh·NH_2 in boiling C_5H_5N affords a *phenylhydrazone*, $C_{22}H_{15}ON_3$, m.p. 224—225°; Hope's degradation product does not react with P_2S_5. (I) is converted by Br in AcOH at 100° into the *lactam*, m.p. 257°, of *x*-bromo-2-*o*-carboxyphenyl-1 : 2 : 3 : 4-tetrahydroquinoline-4-carboxylic acid, oxidised by $KMnO_4$ in alkaline solution to *o*-$C_6H_4(CO_2H)_2$ and oxidised by CrO_3 in AcOH to the *lactam* (**IV**), m.p. 202°, of *x*-bromo-4-keto-2-*o*-carboxyphenyl-1 : 2 : 3 : 4-tetrahydroquinoline (phenylhydrazone, m.p. 247—248°; *CHPh* derivative, m.p. 231—232°). (**IV**) is converted by Br in hot $CHCl_3$ followed by C_5H_5N into the *lactam*, m.p. 261°, of *x*-bromo-4-keto-2-*o*-carboxyphenyl-1 : 4-dihydropyridine, showing that Br is not attached to $C_{(2)}$ of the quinoline nucleus; in AcOH this gives a perbromide which gradually passes into the *lactam*, m.p. 272°, of *x* : 3-dibromo-4-keto-2-*o*-carboxyphenyl-1 : 4-dihydroquinoline. (I) is converted by short ebullition with HNO_3 (*d* 1·4) into the *lactam*, m.p. 260° (decomp.), of *x*-nitro-2-*o*-carboxyphenyl-1 : 2 : 3 : 4-tetrahydroquinoline-4-carboxylic acid, oxidised by CrO_3 in AcOH to the (?) *lactam*, m.p. 309—310°, of *x*-nitro-4-keto-2-*o*-carboxyphenyl-1 : 4-dihydroquinoline and a substance which gives a *phenylhydrazone*, $C_{22}H_{18}O_3N_4$, m.p. 264°. (**II**) and boiling HNO_3 (*d* 1·4) yield the *lactam*, m.p. 253°, of 3-nitro-4-keto-2-*o*-carboxyphenyl-1 : 4-dihydroquinoline. (**II**) is converted by boiling KOH–MeOH into a (?) *polymeride*, m.p. 310°. With *o*-NO_2·C_6H_4·CHO and a little piperidine at 170° (**II**) gives the *o-nitrobenzylidene* derivative, m.p. 262°, which could not be satisfactorily reduced by Zn, Sn, or $SnCl_2$ in acid solution or by Zn–Hg. Condensation with *o*-NHAc·C_6H_4·CHO leads to the *o-acetamidobenzylidene* compound, m.p. 283°, hydrolysed and decyclised by boiling conc. HCl to the *compound*, $C_{23}H_{18}O_3N_2,H_2O$, m.p. 185°. With *o*-NH_2·C_6H_4·CO_2H at 170° (**II**) gives a polymerised *product*, $C_{32}H_{16}O_3N_2$, m.p. >360°, analogous to the product, $C_{32}H_{20}O_2N_2$, m.p. 375°, obtained from (I) and S at 375°. H. W.

Steric factors in quaternary salt formation. W. G. Brown and S. Fried (*J. Amer. Chem. Soc.*, 1943, **65**, 1841—1845).—Methiodides and ethiodides of *N*-methyl-indoline and -tetrahydroquinoline at 45° are formed much faster than those of *N*-methyltetrahydrohomo*iso*-quinoline. Hindrance thus occurs when the two rings are not planar. Similarly, with monocyclic bases there is hindrance when the groups attached to the C_6H_6 ring cannot assume co-planarity with it; thus, the relative effects of substituents reported by Evans *et al.* (A., 1939, I, 527) are the same as their effectiveness in preventing free rotation in the Ph_2 series; also formation of *o*-$C_6H_4Bu^{\gamma}$·NMe_3I is very slow. Attack of the RI occurs at the free electrons and is easier if these are exposed. Relative rates of formation of methiodides of 2 : 6 : 1-$C_6H_3Me_2$·NMe_2, 4 : 3 : 1-NO_2·C_6H_3Me·NMe_2, m.p. 83°, 2-*nitro*-NN-*dimethyl*-m-5-*xylidine* (Me = 1; prep. from the Br-compound by $NHMe_2$ at 100—120°), m.p. 111°, are inconclusive. *E* and log *PZ* are also recorded. R. S. C.

Aminoacridines: some partition and surface phenomena. A. Albert, R. Goldacre, and E. Heymann (*J.C.S.*, 1943, 651—654).—The results obtained from measurements of oil–H_2O partition coeffs. and air–H_2O surface activities of a no. of aminoacridines suggest that marked oleophilic and surface-active properties are unnecessary for, and if present in high degree are inimical to, the development of good antiseptic properties in this series. The following are described: 2-*chloro*-5-*amino*-7-*methoxyacridine*, m.p. 271°, and the *hydrochlorides* of 5-*butyl*-, m.p. 189—190°, -cyclo*hexyl*-, m.p. 271°, *-heptyl-* (+H_2O), m.p. 106°, *-dodecyl-* (+H_2O), m.p. 92°, and *-hexadecyl-aminoacridine* (+H_2O), m.p. 99—100°. F. R. S.

***N*-Substituted 6-chloro-9-amino-2-methoxyacridines.** J. H. Burckhalter, E. M. Jones, W. F. Holcomb, and L. A. Sweet (*J. Amer. Chem. Soc.*, 1943, **65**, 2012—2015).—CH_2:CH·CN and the appropriate amine at the b.p. or 100°/>1 atm. give *β-di*-n- (90%), b.p. 104—105°/10 mm., and -iso-*propyl*- (12%), b.p. 100—102°/13 mm., and *β-di*-n- (96%), b.p. 127—131°/11 mm., and -iso-*butyl*- (51%), b.p. 116—117°/10 mm., *β*-n-*amyl*- (88%), b.p. 112—113°/10 mm., *β-di*-n-*octyl*- (80%), b.p. 180—182°/2 mm., *β-di-β′-ethyl*-n-*hexyl*- (65%), b.p. 163—164°/2 mm., *β*-ethyl-*β′*-hydroxyethyl- (72%), b.p. 133—134°/7 mm. (*picrate*, m.p. 72—74°), and *β-N-β′*-hydroxyethyl-*N*-*n*-butyl- (61%), b.p. 147—148°/7 mm. (*picrate*, m.p. 62—63°), *-propionitrile*. The following are recorded: *γ*-di-*n*-, b.p. 91—93°/15 mm. (*dipicrate*, m.p. 180—181°), and *-iso*-propyl-, b.p. 98—99°/15 mm. [*dipicrate*, m.p. 211—213° (decomp.)], *γ*-di-*n*-, b.p. 121—123°/16 mm. (*dipicrate*, m.p. 182—184°), and *-iso*-butyl-, b.p. 104—108°/10 mm. [*dipicrate*, m.p. 190—192° (decomp.)], *γ-n*-amyl-, b.p. 102—103°/15 mm. (*dipicrate*, m.p. 173—174°), *γ*-ethyl-*β′*-hydroxyethyl-, b.p. 130—131°/15 mm., and *γ-N-β′*-hydroxyethyl-*N*-*n*-butyl-*n*-propylamine, b.p. 147—148°/15 mm. *o*-$C_6H_4(CO)_2N$·$[CH_2]_3$·Br and *p*-NH_2·C_6H_4·NMe_2 at 120—130° give N-*γ*-*p-diethylaminoanilino*-n-*propylphthalimide*, m.p. 106—107°, converted by 85% N_2H_4,H_2O in boiling EtOH into *p*-NEt_2·C_6H_4·NH·$[CH_2]_3$·NH_2, an oil. 6 : 9-Dichloro-2-methoxyacridine and the appropriate diamine, some-

times with K_2CO_3, in PhOH at 100° give 6-chloro-9-γ-di-*n*- (45%) [*dihydrochloride*, $+H_2O$ m.p. 228—229° (decomp.)], and -*iso*-propyl- (62%) [*dihydrochloride*, $+H_2O$, m.p. 227—230° (decomp.)], -9-γ-di-*n*- (50%) (*dihydrochloride*, $+H_2O$, m.p. 200—201°), and -*iso*-butyl- (73%) [*dihydrochloride*, $+H_2O$, m.p. 219—221° (decomp.)], -9-γ-*n*-*amyl*- (65%), m.p. 90—91°, -9-γ-di-*n*-amyl- (63%) (*dihydrochloride*, $+H_2O$, m.p. 165—166°), -9-γ-ethyl-β′-hydroxyethyl- (65%) [*dihydrochloride*, $+H_2O$, m.p. 246—247° (decomp.)], -9-γ-*N*-β′-hydroxyethyl-*N*-*n*-butyl- (53%) (*dihydrochloride*, $+H_2O$, m.p. 180—182°), -9-γ-*p*-diethylaminoanilino- (79%) [*dihydrochloride*, m.p. 185° (decomp.)], -9-γ-β′-diethylaminoethoxy- (40%) [*dihydrochloride*, $+H_2O$, m.p. 221—222° (decomp.)], -9-γ-2′-*amino*-4′-*pyrimidylamino*- (75%), m.p. 221—222°, -9-γ-6′-methoxy-8′-quinolylamino- (76%) [*dihydrochloride*, $+H_2O$, m.p. 241—242° (decomp.)], -9-γ-6′-*chloro*-2′-*methoxy*-9′-*acridylamino*- (72%), m.p. 189—190° (decomp.), and -9-γ-6′-*chloro*-2′-*methoxy*-9′-*acridylamino*-ββ-*dimethyl*- (60%), $+H_2O$, m.p. 112—113°, -*propylamino*-2-*methoxyacridine*, 6-chloro-9-β-hydroxyethyl- (55%), m.p. 201—202° (lit., 191—192°), -9-β-chloroethyl- (64%) [*hydrochloride*, m.p. 265° (decomp.)], -9-*carboxymethyl*- (58%), m.p. 248° (decomp.), -9-3′-*pyridyl*- (57%), $+H_2O$ (lost at 150°), m.p. 202—203° (decomp.), -9-ζ-2′-*amino*-4′-*pyridylamino*-n-*hexyl*- (80%), m.p. 217—220° (decomp.), -9-δ-6′-methoxy-8′-quinolylamino-*n*-butyl- (48%) (*dihydrochloride*, $+H_2O$, m.p. 231—233°), -9-ε-6′-methoxy-8′-quinolylamino-*n*-amyl- (55%) [*hydrochloride*, $+H_2O$, m.p. 135—138° (decomp.)], -*amino*-2-*methoxyacridine*, and 6-*chloro*-9-*anilino*- (65%), m.p. 199—201°, -9-p-*dimethylaminoanilino*- (66%), m.p. 187—188°, -9-p-*diethylaminoanilino*- (48%), m.p. 127—129° (decomp.), and -9-p-*anisidino*- (79%), m.p. 177—179°, -2-*methoxyacridine*. R. S. C.

Attempts to prepare optically active tervalent nitrogen compounds. II. 1 : 9-(2′ : 3′ : 4′ : 5′-Tetrahydrophenylene)carbazole. R. W. G. Preston and S. H. Tucker (*J.C.S.*, 1943, 659—661).—9-Aminocarbazole (*picrate*, m.p. 136—138°) and *cyclo*hexanone give *cyclo*hexanonediphenylenehydrazone (cf. Manjunath, A., 1927, 978), which with dry HCl in tetralin affords 1 : 9-(2′ : 3′ : 4′ : 5′-*tetrahydrophenylene*)*carbazole*, m.p. 99—100° [*s*-$C_6H_3(NO_2)_3$ *compound*, m.p. 164—166°; *picrate*, m.p. 159—160°], dehydrogenated (S) to 1 : 9-phenylenecarbazole, m.p. 136·5—138·5°. This compound is synthesised by diazotisation (in H_2SO_4–AcOH) of 1-*amino*-, m.p. 96—98°, obtained by reduction (Na_2S–EtOH) of 1-*nitro*-9-*phenylcarbazole*, m.p. 130—132°, which is prepared from 1-nitrocarbazole, PhI, K_2CO_3, and Cu. 3-*Nitro*-9-*phenylcarbazole*, m.p. 140—142°, and the *diphenylenehydrazones* of $AcCO_2H$, m.p. 157—160° (decomp.) [lit., 148—150° (decomp.)], $AcCO_2Me$, m.p. 89—90°, $CH_2Ac{\cdot}CO_2Et$, m.p. 113°, Et oxaloacetate, m.p. 85—87°, and $COMe_2$, m.p. 78—81°, are described. F. R. S.

4-Amino-2-methyl-5-β-bromoethylpyrimidine hydrobromide. J. M. Slobodin (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, **39**, 237—238).—In the compound $C_6H_{10}N_3Br_3$ all 3 Br are titrated with $AgNO_3$, so that the bond $CH_2{\cdot}Br$ must be nearly dissociated. J. J. B.

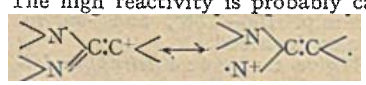
Sulphonamidopyrimidines.—See B., 1944, III, 18.

Pharmacological properties of simple compounds of histamine with amino-acids. M. Rocha e Silva (*J. Pharm. Exp. Ther.*, 1943, **77**, 198—205).—See A., 1944, III, 211. The following are described: *acetyldehydrophenylalanyl*- [α-*acetamidocinnamyl*-], m.p. 134—137°, *acetyl*-dl-*phenylalanyl*-, m.p. 95—100°, *benzoyl*-l-*tyrosyl*-, m.p. 140—146°, *carbobenzyloxy*-l-*tyrosyl*-, m.p. 147°, *carbobenzyloxy*-l-*leucylhistamine*, m.p. 113—117°.

Preparation of sulphanilamidoindazoles. C. E. Kwartler and P. Lucas (*J. Amer. Chem. Soc.*, 1943, **65**, 1804—1806).—6-Amino-, m.p. 209—210°, is rapidly obtained from 6-nitro-indazole by H_2–Raney Ni in MeOH at 50°/30 atm. *o*-$CN{\cdot}C_6H_4{\cdot}N_2Cl$ and $SnCl_2$–conc. HCl give 3-aminoindazole. *p*-$NHAc{\cdot}C_6H_4{\cdot}SO_2Cl$ with the appropriate aminoindazole in $COMe_2$ or C_5H_5N gives 3-, m.p. 253—255°, 5-, m.p. 250—252°, 6-, m.p. 245—246°, and -7-N^4-*acetylsulphanilamidoindazole*, m.p. 258—260°, hydrolysed by aq. acid or alkali or 20% HCl–EtOH to 3-, m.p. 225—226°, 5- (**I**), m.p. 247—248°, 6- (**II**), m.p. 195—196°, and 7-*sulphanilamidoindazole*, m.p. 254—256°, respectively. These have bacteriostatic action; some are bactericidal and show promise against *Streptococcus hæmolyticus* and *Pneumococcus* in mice. (**I**) and (**II**) are, respectively, 2 and 3—4 times as effective as *p*-$NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$ against *Streptococcus*. R. S. C.

(A) **Allylic character of 2-α-chloroalkylbenziminazoles.** H. Skolnik, J. G. Miller, and A. R. Day. (B) **Reaction of 2-α-chloroalkylbenziminazoles with potassium iodide in acetone solution.** H. Skolnik, A. R. Day, and J. G. Miller (*J. Amer. Chem. Soc.*, 1943, **65**, 1854—1858, 1858—1862).—(A) 2-α-Chloroalkylbenziminazoles are even more reactive than the usual allyl chloride types (cf. A., 1939, II, 285; 1941, II, 150). 2-Chloromethylbenziminazole (**I**), m.p. (at 1° per min.) 159—160° or (at 2° per min.) >250° (after changing to a yellow solid at 140°; ? polymerisation), with MgPhBr in Et_2O or boiling KCN–EtOH–H_2O gives gums, in boiling H_2O (45 min.) gives 2-hydroxy- (94%), m.p. 170·5—171·5° [also obtained from *o*-$C_6H_4(NH_2)_2$ (**II**) and $OH{\cdot}CH_2{\cdot}CO_2H$], with KI in boiling $COMe_2$ gives 2-*iodo-methylbenziminazole* (31%), m.p. 137—139° (decomp.), and with boiling NaOEt–EtOH gives 1 : 2-4 : 5-*di*-1′ : 2′-*benziminazolopiperazine* (73%), m.p. >300°, but is unchanged by boiling EtOH or $NPhMe_2$– or C_5H_5N–EtOH. 2-*Ethoxymethylbenziminazole*, m.p. 154·5—155°, is obtained (88%) from (**II**) and $OEt{\cdot}CH_2{\cdot}CO_2H$. 2-α-Chloro- (**III**), m.p. 134—135°, in boiling H_2O (10 min.) gives 2-α-hydroxy-ethylbenziminazole (70·6%), m.p. 179—180°, and 2-α-*chloro*- (**IV**), m.p. 144·5—145·5°, gives similarly 2-α-*hydroxy*-n-*propylbenziminazole*, m.p. 220—221° [whence (**IV**) is prepared by $SOCl_2$–$CHCl_3$]; the products are also obtained from (**II**) by $OH{\cdot}CHMe{\cdot}CO_2H$ or $OH{\cdot}CHEt{\cdot}CO_2H$ (prep. from $OH{\cdot}CHEt{\cdot}CN$ by conc. HCl at room temp. and then 60—70°), respectively. 2-α-*Chloroisopropylbenziminazole* (**V**), m.p. 135·5—136·6°, is hydrolysed to the 2-α-*OH*-compound, m.p. 227·5—228° [prepared from (**II**) by $OH{\cdot}CMe_2{\cdot}CO_2H$ and giving (**V**) with $SOCl_2$–$CHCl_3$], by evaporating its solution in $COMe_2$ containing a little H_2O in a stream of air at room temp., and with a little C_5H_5N in boiling EtOH gives 2-α-*ethoxyisopropylbenziminazole* (56%), $+H_2O$ (retained at 130°), m.p. 203·7—204·4°. *o*-$NH_2{\cdot}C_6H_4{\cdot}NHMe$,2HCl (**VI**) and $CH_2Cl{\cdot}CO_2H$ in boiling 2N-HCl give 1-*methyl*-2-*chloro*- (**VII**) (58%), m.p. 94·5—95·5°, which with KCN–$COMe_2$–H_2O gives 1-*methyl*-2-*cyano-methylbenziminazole* (80%), m.p. 239—240°. $OH{\cdot}CHMe{\cdot}CO_2H$ and (**VI**) give 1-*methyl*-2-α-*hydroxy*-, m.p. 59·6—61°, and thence ($SOCl_2$–$CHCl_3$) 1-*methyl*-2-α-*chloro-ethylbenziminazole* (**VIII**), m.p. 64—65°. M.p. are corr.

(B) Interaction of 2-α-chloroalkylbenziminazoles with KI in $COMe_2$ proceeds to conclusion as a bimol. reaction. *k* is measured at 25° by the method of Conant *et al.* (A., 1924, i, 273), but not by other methods. It is const. for given concns. but increases greatly as the concn. of the Cl-compound decreases. Relative *k* vals. are (**I**) < (**III**) < (**IV**) < (**VIII**) < (**V**) < (**VII**); all are $\gg k$ for $CH_2{:}CH{\cdot}CH_2Cl$ or CH_2PhCl, which are similarly affected by concn. The high reactivity is probably caused by resonance of the type,



R. S. C.

Diels–Alder synthesis with 2 : 3-dimethylquinoxaline. Reaction between maleic anhydride and anthranil. A. Schonberg and A. Mostafa (*J.C.S.*, 1943, 654—656).—2 : 3-Dimethylquinoxaline (**I**) and $(CH{\cdot}CO)_2O$ form a 1 : 1 additive *product*, m.p. >305°; *p*-benzoquinone in PhMe gives a 2 : 1 additive *product*, m.p. 190°. Alternative formulæ are suggested for the products. No reaction of this kind is observed between (**I**) and $(CH_2{\cdot}CO)_2O$ or between (**II**) or *p*-benzoquinone and quinoxaline or its derivatives not capable of forming a diene system. *o*-$C_6H_4(NH_2)_2$ and (**II**) give an additive *product*, $C_{14}H_{12}O_6N_2$, m.p. 189—190°, and an additive *product*, m.p. ~150°, (some decomp.), is formed from 1 : 1 mol. proportions of (**II**) and anthranil. F. R. S.

Heterocylic nitrogen compounds. I. Derivatives of 7 : 16-diazanaphthacene. H. H. Hatt and (Miss) E. F. M. Stephenson (*J.C.S.*, 1943, 658—659).—Phthalaz-1 : 4-dione and *o*-$C_6H_4(CH_2Br)_2$ at 215—220° give 6 : 17-*diketo*- 6 : 8 : 15 : 17-*tetrahydro*-7 : 16-*diazanaphthacene*, m.p. 196·5—197·5°, in 65% yield [also obtained from *o*-$C_6H_4(COCl)_2$ and 1 : 2 : 3 : 4-tetrahydrophthalazine hydrochloride (**I**)], which with NaOEt–EtOH affords the *Na* salt of 2-o-*carboxybenzoyl*-1 : 2 : 3 : 4-*tetrahydrophthalazine* (+2·5H_2O). 3 : 1 : 2-$NO_2{\cdot}C_6H_3(COCl)_2$ and (**I**) in C_5H_5N yield 1-*nitro*-6 : 17-*diketo*-6 : 8 : 15 : 17-*tetrahydro*-7 : 16-*diazanaphthacene*, m.p. 249—250° (slight decomp.), reduced ($SnCl_2$–HCl) to the 1-NH_2-compound, m.p. 185—187° (decomp.) [*Bz* derivative, m.p. 260—261° (slight decomp.)]. 4 : 1 : 2-$C_6H_3Cl(CO)_2NH$, N_2H_4, and EtOH give 6-*chlorophthalaz*-1 : 4-*dione*, m.p. 348—350° (sealed tube). F. R. S.

Ichthyopterin, the blue-fluorescent substance of fish skin. R. Hüttel and G. Sprengling (*Annalen*, 1943, **554**, 69—82).—The presence of blue or green fluorescence in fish skins appears to be a family property; green or no fluorescence is observed in species without or with slightly developed scales. The intact skin of *Phoxinus laevis*, Ag, is not fluorescent but slight injury induces this phenomenon. If the fish is killed without other damage, fluorescence appears slowly after 1—2 hr. Alcohols, 1% CH_2O, and urethane solution cause almost immediate death with simultaneous appearance of fluorescence. Dil. acids and alkalis induce fluorescence only if the animal is so hurt that it dies within 15 min. The activity of neutral salts depends on the anion; only univalent ions induce fluorescence. The skins of freshly-killed *Leuciscus rutilus*, *Scardinius erythrophthalamus*, and *Blicca bjorkna* are pre-extracted and preserved by EtOH and then extracted several times with dil. AcOH. The conc. extracts are pptd. with EtOH, and Ca is removed as CaC_2O_4. The remaining solution is treated with $Pb(OAc)_2$ at pH 8—9, the ppt. is decomposed with H_2SO_4, and the fluorescent material is eluted from the $PbSO_4$ by C_5H_5N–H_2O. It is purified first by use of NH_3 and finally through the Na H salt, thereby giving *ichthyopterin* (**I**), probably $C_7H_8O_3N_4$. Spectroscopically (**I**) is similar to but distinct from leucopterin and almost identical with "anhydroleucopterin" (8-deoxyleucopterin) (**II**). Like (**II**) it shows the characteristic "redox" reaction with

fuming HI. Fluorescences of (I) and (II) are identical in colour, in dependence on pH, and, generally, in intensity. However, (I) and (II) are certainly not identical. Very probably (I) is the chromophor of (II) and therefore a derivative of 9-hydroxypteridin. H. W.

Constitution of yeast-ribonucleic acid. VI. Nature of the carbohydrate radicals. J. M. Gulland and G. R. Barker (*J.C.S.*, 1943, 625—628).—Examination of the evidence on which the conclusion that *d*-ribose is the carbohydrate of yeast-nucleic acid (I) and the related nucleotides is based shows it to be unsatisfactory. *d*-Ribose, and *l*-lyxose in small amount, have been identified, by oxidation and conversion into benziminazoles, in the products of hydrolysis of (I), and *d*-ribose has been similarly identified as the carbohydrate of guanylic, adenylic, and cytidylic acids prepared from (I), which is therefore designated correctly as the ribonucleic acid of yeast. d-*Ribobenziminazole*, m.p. 239—240°, $[\alpha]_D^{20}$ −50·4° in 5% aq. citric acid [lit. m.p. ~190° (decomp.), $[\alpha]_D^{20}$ +21·6°], has been prepared from synthetic *d*-ribonic acid. d(−)-*Arabinose*-2 : 4-*dinitrophenylosazone*, m.p. 259—260°, is identical with that obtained from (I). F. R. S.

Chlorophyll *d*, a green pigment of red algæ. W. M. Manning and H. H. Strain (*J. Biol. Chem.*, 1943, **151**, 1—19).—Various species of red algæ contain, in addition to chlorophyll *a* (I), a second green pigment containing Mg, *chlorophyll* d (II). Chlorophyll *b* or *c* is not found in these algæ. (II) is most easily prepared by adsorption of the pigments obtained by the partial extraction of *Sigartina agardhii*. Max. light absorption by (II) occurs at λ longer than that of the max. of (I); in MeOH the max. absorption for (II) is at 696 mμ., and for (I) at 665 mμ. Absorption at long λ by (II) may extend by 30 mμ. the range of light used in photosynthesis. (II) is converted, rapidly when heated or slowly at room temp., into a mixture containing three isomerides in addition to unaltered material. One of these isomerides, *chlorophyll* d′, has an absorption spectrum very similar to that of (II) whereas the other two, iso*chlorophyll* d (III) and iso*chlorophyll* d′, have spectra resembling that of (I). The isomerides are reconvertible into (II). Treatment of (II) with acid removes the Mg and forms a mixture of two interconvertible phæophytins. At −80° treatment with acid produces mainly the labile, yellow-brown *phæophytin* d (IV); at room temp., grey iso*phæophytin* d (V) is the principal product. (IV) is rapidly converted into (V) when it is treated with acid at room temp. (III) yields (V) when treated with acid at room temp. or −80°. (V) is remarkably similar to phæophytin *a* in its absorption spectrum and in its adsorbability on powdered sugar. With Grignard's reagent (V) produces (III) but little or no (I). Neither (II) nor (III) is formed when (IV) is treated with Grignard's reagent. The same final product is formed in each case when (II) and its isomerides are treated successively with alkali and acid. When treated in this manner (I) gives a product distinctly different from that derived from (II). H. W.

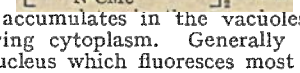
Effect of pH changes on the properties of sodium thymonucleate solutions. C. F. Vilbrandt and H. G. Tennent (*J. Amer. Chem. Soc.*, 1943, **65**, 1806—1809).—η of 0·3% Na thymonucleate solution (pH 5·6) containing 1% of NaCl decreases gradually as the pH is changed to 2·6 or 11·6. Subsequent neutralisation raises η, but not to the original val. and the recovery is slow. Sedimentation and diffusion experiments connect these changes with dc- and re-polymerisation; the range of mol. wts. after re-polymerisation is it was originally and some of the newly formed mols. are very large. Isolation of nucleic acids will thus give altered substances unless it is conducted in neutral solution. R. S. C.

Quaternary cetylammonium compounds.—See B., 1943, III, 308.

Interaction of *o*-quinones and *o*-quinoneimines with primary amines. G. McCoy and A. R. Day (*J. Amer. Chem. Soc.*, 1943, **65**, 1956—1959).—Retenequinone (I) with $CH_2R{\cdot}NH_2$ (R = Pr$^\alpha$, OH·CH_2, or Ph) in EtOH, PhMe, etc. at 70—100° gives 40—80% yields of 2-substituted reteneoxazoles, but with CHPhMe·NH_2 or NH_2Pr^β gives gums (cf. Bamberger *et al.*, A., 1885, 905; Pschorr, A., 1902, i, 672). Reaction proceeds by way, of successively, (i) the Schiff's base, (ii) 9-alkylideneamino-10-hydroxy-compound, and (iii) 2 : 3-dihydro-oxazole, which is oxidised by unchanged (I). Step (i) is proved by isolation of H_2O when the reaction is effected in PhMe and by evolution of NH_3 when retenequinonemonoimine (II) replaces (I). Step (ii) is proved by formation of PhCHO when a reacting mixture of (I) and $CH_2Ph{\cdot}NH_2$ is treated with HCl and by the fact that 9-amino-10-phenanthrol with Pr$^\alpha$CHO or PhCHO gives 2-*n*-propyl- and 2-phenyl-phenanthroxazole (III), respectively. The final oxidation by (I) is proved by adding *p*-O:C_6H_4:O, which finally appears as quinol and quinhydrone. That yields exceed 100% is due to the ready re-oxidation of retencquinol. Liberation of NH_3 from (II) proves that reaction occurs at the NH. Yields from (II) are > those from (I), because side-reactions due to H_2O are eliminated. Phenanthraquinone and $CH_2Ph{\cdot}NH_2$ in boiling PhMe give (III) (9%), 2-*phenyl*-1-*benzylphenanthriminazole* (IV) (2·7%), m.p. 241—241·5°, and PhCHO, but in boiling AcOH give 48% of *phenanthroxazine*, m.p. >360°, with 14% of (III) and 4% of (IV); NH_2Bu^α gives only gums. Phenanthraquinonemonoimine with $CH_2Ph{\cdot}NH_2$ or NH_2Bu^α in PhMe gives (III) (59%) and 2-propylphenanthroxazole (35%), respectively. 2-*Hydroxymethylreteneoxazole*, m.p. 187·5—189° (*acetate*, m.p. 134·5—136°), is described. R. S. C.

Vitamin-B_1. 4-Methyl-5-β-hydroxyethylthiazole. J. M. Slobodin and E. E. Gelms (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, **39**, 152—154).—In Buchman's synthesis (A., 1936, 1394) of 4-methyl-5-β-hydroxyethylthiazole some 4-*methyl*-5-α-*hydroxyethylthiazole*, b.p. 121—122·5°/2 mm. (*picrate*, m.p. 91°), is also produced. J. J. B.

2-Amino-4 : 5-trimethylenethiazole.—See B., 1944, II, 35.

Photosynthesis of a fluorescent substance of the thiazole series (vitachrome). P. Karrer and M. C. Sanz (*Helv. Chim. Acta*, 1943, **26**, 1778—1784).—Exposure of crude 4-methyl-5-β-hydroxyethylthiazole (I) in 1% aq. solution at pH 8 to ultra-violet light followed by chromatographic purification leads to the isolation of *vitachrome* (II) in 1—3% yield. (II) does not arise from (I) which has been purified through the picrate and its production is due to the presence in (I) of small amounts of 2-*chloro*-4-*methyl*-5-β-*hydroxyethylthiazole* (III), b.p. 88—92°/0·002—0·003 mm., which does not form a picrate, gives a viscous *acetate*, and is converted by anhyd. KOAc in AcOH followed by hydrolysis with 10% H_2SO_4 into 2-*keto*-4-*methyl*-5-β-*hydroxyethyl*-2 : 3-*dihydrothiazole*, m.p. 132—133°. Fluorescence is observed sooner in the irradiation of crude (I) than in that of (III) but the difference disappears after a few hr. (II) has m.p. 175° (corr.). The crystals have a pale yellow-green fluorescence in ultra-violet light, in which the aq. solution appears a very intense pale blue. (II) gives a cryst. *diacetate* with a very marked, pale blue fluorescence and is probably  . (II) diffuses very rapidly into the cell, accumulates in the vacuoles, and is frequently fixed by the living cytoplasm. Generally it is the neighbourhood of the cell nucleus which fluoresces most strongly. No harmful effects have been noticed. It appears completely non-toxic to small animals and to pass unchanged through the kidneys. H. W.

Pyrazolones, benzthiazoles, etc.—See B., 1943, II, 400.

Cyanines.—See B., 1944, II, 10.

Photographic sensitisers.—See B., 1944, II, 57, 58.

Miscellaneous heterocyclic compounds.—See B., 1944, II, 7.

VII.—ALKALOIDS.

Ergot alkaloids. IX. Dihydro-derivatives of the natural, lævorotatory ergot alkaloids. A. Stoll and A. Hofmann (*Helv. Chim. Acta*, 1943, **26**, 2070—2081).—Lævorotatory ergot alkaloids (I) are converted into homogeneous H_2-derivatives (II) in good yield by hydrogenation at 60°/35 atm. in dioxan containing Pd sponge. They differ so little from (I) in cryst. form, solvent of crystallisation, and solubility that it may be assumed that hydrogenation does not cause any marked change in the configuration of the mols. With org. and inorg. acids (II) generally give stable, well-cryst. salts. (II) scarcely show the intense blue fluorescence in the ultra-violet which is characteristic of (I) but the dark blue Keller colour reaction is retained. The following are described: *dihydroergotamine*, $C_{33}H_{37}O_5N_5,2COMe_2,2H_2O$, m.p. 239° (decomp.), $[\alpha]_D^{20}$ −64°, $[\alpha]_{5461}^{20}$ −79° in C_5H_5N [*hydrochloride*, m.p. 220—225° (decomp.); *methanesulphonate*, m.p. 230—235° (decomp.); normal *tartrate*, m.p. 210—215° (decomp.)]; *dihydroergosine*, m.p. 212° (decomp.), $[\alpha]_D^{20}$ −52°, $[\alpha]_{5461}^{20}$ −64° in C_5H_5N; *dihydroergocristine*, m.p. 180° (decomp.) from $COMe_2$, 200° from C_6H_6, $[\alpha]_D^{20}$ −56°, $[\alpha]_{61}^{20}$ −68° in C_5H_5N; *dihydroergocryptine*, m.p. 235° (decomp.), $[\alpha]_D^{20}$ −41°, $[\alpha]_{5461}^{20}$ −52° in C_5H_5N; *dihydroergocornine*, m.p. 185—187° (decomp.), $[\alpha]_D^{20}$ −48° in C_5H_5N. (II) are far more stable than (I) towards light, oxidising influences, acids, and alkalis. These properties are shared by d(−)-*dihydrolysergic acid* (III), decomp. >300°, darkens at 250°, $[\alpha]_D^0$ −122°, $[\alpha]_{5461}^{20}$ −146° in C_5H_5N, obtained from them by alkaline hydrolysis. Fission of (II) by N_2H_4 leads without racemisation or isomerisation to d(−)-*dihydrolysergHydrazide*, m.p. 247° (decomp.), $[\alpha]_D^{20}$ −123°, $[\alpha]_{61}^{20}$ −147° in C_5H_5N, hydrolysed by alkali to (III). Saturation of the double linking in (I) causes complete disappearance of the reaction towards the uterus and a great diminution in toxicity but the neurovegetative action is retained and in certain cases is enhanced. M.p. are corr. Diagrams of apparatus and photomicrographs of (II) are given. H. W.

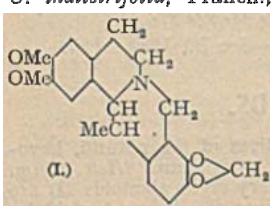
Synthesis in the series of cinchona alkaloids. IV. Homomeroquinine and the partial synthesis of quinotoxine. M. Prostenik and V. Prelog (*Helv. Chim. Acta*, 1943, **26**, 1965—1971).—Technical cinchonine is purified by $Hg(OAc)_2$ and successively treated with 50% H_2SO_4 at 140°, benzoylated in presence of K_2CO_3 and $CHCl_3$, and treated with NH_2OH, thereby giving a mixture of stereoisomeric *N*-benzoylcinchotoxineoximes, m.p. 65—95°. This is transformed by *p*-$C_6H_4Me{\cdot}SO_2Cl$ and NaOH into a mixture of amides,

hydrolysed by alkali to homomeroquinine, isolated as the *Et* ester, b.p. 102—104°/0·1 mm., $[\alpha]_D^{18}$ +42·2° in 96% EtOH [*aurichloride*, m.p. 110·5—112° (decomp.); N-*Bz* derivative (I), b.p. 190—194°/0·1 mm., which rapidly becomes discoloured when kept]. This is hydrolysed by alkali to the free *base*, m.p. 211—212° (decomp.), $[\alpha]_D$ +50·4° in H_2O [normal *dibenzoyl*-d-*tartrate*, m.p. 186° (decomp.); *reineckate*, m.p. 131·5—132°]. N-*Methylhomomeroquinine Et ester*, b.p. 135—140°/23 mm., $[\alpha]_D^{16.5}$ +30·3° in EtOH, results similarly from *N*-methylcinchotoxincoxime. (I) is condensed with Et quinate by dry NaOEt at 80—90° and the product is hydrolysed to quinotoxine [normal *dibenzoyl*-d-*tartrate*, m.p. 183° (decomp.), $[\alpha]_D^{20}$ −16·0° in EtOH–$CHCl_3$ (1 : 2), identical with the product obtained from quinine; *dipicrolonate*, m.p. 210° (decomp.)], transformed into a mixture of stereoisomeric benzoylquinotoxineoximes, m.p. 65—95°. H. W.

10-Iodohydroquinines. (Miss) A. G. Renfrew, C. L. Butler, and L. H. Cretcher (*J. Amer. Chem. Soc.*, 1943, **65**, 2038—2039).—*iso*Quinine and HI (*d* 1·7) at 100° give 10-iodohydroquinine, α-, $[\alpha]$ −218°, and α′-form, anhyd., m.p. 130°, $[\alpha]_D$ −22·3°, and +C_6H_6, $[\alpha]$ −19° (cf. Suszko *et al.*, A., 1936, 490, 870). Rotations in (?) EtOH. R. S. C.

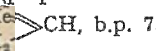
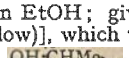
Berberine content of *Coscinium fenestratum* (Colebr.). R. Child and W. R. N. Nathaniel (*Current Sci.*, 1943, **12**, 255—256).—Extraction of the air-dried stems (H_2O, 6·8%) of Ceylonese material with 95% EtOH removes 9·2% of material and from the alcoholic extract berberine is readily pptd. as the H sulphate (yield of crude salt ~4·1%) by a slight excess of H_2SO_4. The residue from the evaporated filtrates is treated with H_2O and then with Et_2O, which removes 4·1% of resin. The aq. extract after being made alkaline with NaOH gives crude alkaloids (0·67%) to Et_2O and after saturation with CO_2 0·2% of crude phenolic alkaloids, thus partly confirming the findings of Varier *et al.* (A., 1944, III, 156). The ash, insol. in 2N-HCl, contains CaO 36·8, K_2O 7·6, and Cl′ 0·33%. The high Ca content is noticeable, corresponding with 1·0% of CaO in the original stems. H. W.

Alkaloids of fumariaceous plants. XXXVI. *Corydalis thalictrifolia*, Franch. and constitution of a new alkaloid, thalictrifoline. XXXVII. *Dactylicapnos macrocapnos*, Hutchinson. R. H. F. Manske (*Canad. J. Res.*, 1943, **21**, B, 111—116, 117—118).—XXXVI. *C. thalictrifolia*, Franch., contains protopine, *d*-stylopine (partly racemised), *l*-corypalmine, adlumidine, d-*thalictrifoline* (I), m.p. 155°, $[\alpha]^{25}$ +218° in MeOH, dehydrothalictrifoline, isolated as *hydrochloride* (II), m.p. 271°, and alkaloids *F* 59, $C_{19}H_{20}O_3N(OMe)$, m.p. 176°, largely resolidifying and remelting at 192—200°, and *F* 60, $C_{19}H_{15}O_2N(OMe)$, m.p. 123°. (I)


(I.)

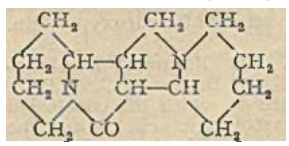
with I and NaOAc in hot EtOH yields a quaternary salt, reduced (Zn + HCl) to the hydrochloride of dl-*thalictrifoline*, m.p. 151°, similarly obtained from (II). Oxidation ($KMnO_4$) of (I) yields *m*-hemipinic acid, but no 3 : 4-methylenedioxyphthalic acid. (I) with dil. H_2SO_4 containing phloroglucinol, followed by methylation and racemisation (by oxidation and reduction), yields *meso*corydaline. All m.p. are corr.

XXXVII. *D. macrocapnos*, Hutchinson, contains protopine, *allo*cryptopine, stylopine, and a considerable amount of fumaric acid, but no phenolic bases. A. Li.

Structure of monocrotaline. IX. Proof of the position of the ethylenic linking in retronecine. R. Adams and J. E. Mahan (*J. Amer. Chem. Soc.*, 1943, **65**, 2009—2012).—The structure of retronecine (A., 1943, II, 113) is confirmed. Deoxyretronecine hydrochloride in $SOCl_2$ at the b.p. gives *chloroisoheliotridene* (83%), b.p. 59·5—60·5°/4·5 mm., $[\alpha]_D^{32}$ +50·10° (homogeneous) [*picrate*, m.p. 179·5—180 (decomp.)], reduced by $CrCl_2$–HCl (prep. *in situ* described) to iso*heliotridene* (88%), $[CH_2]_3$  CH, b.p. 73°/30 mm., $[\alpha]_D^8$ −45·79° (homogeneous) (*picrate*, m.p. 198·5—199·5°), which with H_2–PtO_2 gives heliotridane and, as hydrochloride in H_2O, with O_3 yields 2-*acetylpyrrolidinoacetic acid hydrochloride* (42%), m.p. 180—181°, $[\alpha]_D^{27}$ −4·40° in MeOH [free acid unstable; 2 : 4-*dinitrophenylhydrazone*, m.p. 199—201° (decomp.), titrates as an NH_2-acid hydrochloride; CHI_3 test positive in H_2O]. This is hydrogenated (PtO_2) in EtOH to 2-α-*hydroxyethylpyrrolidinoacetic acid*, m.p. 186·5—187·5°, $[\alpha]_D^8$ −63·47° in H_2O [*hydrochloride* (II), m.p. 147—148°, $[\alpha]^{32}$ −54·31° in EtOH; gives the CHI_3 test] [and some of its lactone (III) (see below)], which with CH_2N_2–Et_2O gives the hygroscopic, oily betaine, 

(*hydrochloride*, softens 170°, m.p. 176—177°). In Ac_2O at 100° (II) gives (III) (*methiodide*, m.p. 242—243°; *picrate*, m.p. 169—170°). M.p. are corr. R. S. C.

Constitution of hydroxypachycarpine. A. P. Orechof, M. I. Kabatschnik, and T. J. Kefeli (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **31**, 335—338).—Hydroxypachycarpine (I) is very resistant towards acids and alkalis but is hydrolysed by conc. HCl at 180° for 15 hr. and the product is esterified to *Et pachycarpate* (II), b.p. 162—166°/2 mm., $[\alpha]_D^{14}$ −12·2° in EtOH, which re-forms (I) when hydrolysed by 50% H_2SO_4. The presence of NH in (II) is established by the isolation of a *Bz* derivative, m.p. 121—122°, and a *NO*-compound, m.p. 86—88°. A lactam group is therefore present in (I) and consequently also in hydroxysparteine. The constitution of (I) is established. H. W.


(I.)

VIII.—ORGANO-METALLIC COMPOUNDS.

Mercuric derivatives of acetamido-acids.—See B., 1944, III, 18.

3-Pyridylmercuric chloride.—See B., 1944, III, 18.

Azo-lead dyes. C. G. Stuckwisch (*Iowa State Coll. J. Sci.*, 1943, **18**, 92—94).—Halogen–metal interconversion studies led to the prep. of $PbPh_3$ *p*-, m.p. 172°, and *o*-amino-, m.p. 164—165°, *p*-methylamino-, m.p. 97—98°, *o*-dimethylamino-, m.p. 101°, and *o*-hydroxyphenyl, m.p. 217—218° (decomp.), and Pb *p*-dimethylaminophenyl Et_3, b.p. 130°/1 mm. (no details given). Organo-Pb compounds containing an azo-linking are preferably prepared from PbR compounds and diazotised amines rather than from diazotised Pb amino-aryl compounds. The following were prepared: $PbPh_3$ 4- and 2-(2′-hydroxy-1′-naphthaleneazo)phenyl, 2-hydroxy-3 : 5-di-(*p*-nitrobenzeneazo)phenyl, 2-hydroxy-5-(*p*-chloro-, -bromo-, -iodo-, and -carboxybenzeneazo)phenyl; 4 : 4′-bis-(4′-hydroxy-3′-triphenylplumbophenylazo)diphenyl; $PbPh_3$ 5-(*p*-nitro-, -chloro-, -bromo-, and -carboxybenzeneazo)-2-dimethylaminophenyl; $PbPh_3$ 4-methoxy-3- and 2-methoxy-5-*p*-nitrobenzeneazophenyl. F. R. G.

IX.—PROTEINS.

Role of glycine in protein structure. H. Neurath (*J. Amer. Chem. Soc.*, 1943, **65**, 2039—2041).—The absence of side-chains in, and free rotation of, glycine allows closer packing of bulky NH_2-acids, readier orientation of polar side-chains at interfaces, and unusual repeating patterns (*e.g.*, in silk fibroin). Glycine is probably present at least in small amounts in all proteins, difficulties in its detection having often led to its being overlooked. The large space-requirements of proline and hydroxyproline in gelatin (~32%) and elastin (~17%) are compensated by large contents (~25% and 29%, respectively) of glycine. R. S. C.

Hydrolysis of proteins and peptones at high temperatures and catalytic effect of metal ions on rate of hydrolysis. F. Licben (*J. Biol. Chem.*, 1943, **151**, 117—121).—Complete hydrolysis of casein is effected by heating a 2% solution in 20% H_2SO_4 for 1 hr. at 160°. Similar data are given for other proteins. The importance of a low initial substrate concn. is stressed. Ti and Sn salts catalyse the reaction appreciably; Cu, Mn, and Ni salts are without effect. Peptones proved more resistant than casein or gelatin. E. C. W.

Influence of sugars on formation of sulphydryl groups in heat-denaturation and coagulation of egg-albumin. C. D. Ball, C. R. Hardt, and W. J. Duddles (*J. Biol. Chem.*, 1943, **151**, 163—169).—Hexoses and pentoses inhibited the formation of SH groups (for determination cf. C., 1944, Part 1) and increased the amount of non-coagulable N when ovalbumin (I) was denatured by heat. This inhibiting influence towards coagulation is not increased by longer contact of the sugar with (I) at a pH of either 4·8 or 8·6. (I) coagulated in presence of glucose yields no more reducing substances after partial hydrolysis than (I) coagulated alone. E. C. W.

Amino-acids yielded by β-lactoglobulin. D. Bolling and R. J. Block (*Arch. Biochem.*, 1943, **2**, 93—95).—Cryst. β-lactoglobulin contained N 15·53, S 1·68, cystine 3·5, arginine 3·2, histidine 1·8, lysine 9·9, tyrosine 4·2, tryptophan 1·9, phenylalanine 5·2, threonine 5·8, *iso*leucine 6·4, valine 6—9, and leucine 13—21%. E. R. S.

Dispersion of keratins. I. Dispersion and degradation of keratins by sodium sulphide. C. B. Jones and D. K. Mecham (*Arch. Biochem.*, 1943, **2**, 209—223).—When the keratin (I) (N 15·7—16·1, H_2O 7—10%) of the freshly plucked feathers of hens is treated with Na_2S, max. dispersion and min. degradation are achieved by using 100 ml. of 0·1M-Na_2S at 30° and digesting for ~2 hr. Approx. quant. recovery of the dispersed material is attained by adjusting the pH to 4·2. (I) of the feathers is more readily dispersed and less stable in solution than are (I) of cattle hooves, wool, and hog's hair. W. McC.

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A II—Organic Chemistry.

APRIL, 1944.

I.—ALIPHATIC.

Modern methods of preparative organic chemistry. XI. Oxidations with selenium dioxide. G. Stein. **XIII. Hydrogenation with Raney catalysts.** R. Schroter. **XIV. Boron fluoride as catalyst of chemical reactions.** D. Kastner (*Angew. Chem.*, 1941, **54**, 146—152; 229—234, 252—260; 273—281, 296—304).—Reviews.

Reaction of hydrogen atoms with propylene. B. S. Rabinovitch, S. G. Davis, and C. A. Winkler (*Canad. J. Res.*, 1943, **21**, **B**, 251—257).—The principal products of the reaction between H atoms and C_3H_6, studied by the Wood–Bonhoeffer method over the temp. range 30—250°, are C_3H_8, C_2H_6, and CH_4. No unsaturated products appear to be formed. The nature and proportions of the products are independent of temp. A mechanism is suggested based on the formation of an active Pr radical as the primary step. H. W.

Action of anisole with *aaa*-trichloro-β-methyl-Δ$^{\beta}$-propene. C. C. Price and H. D. Marshall (*J. Org. Chem.*, 1943, **8**, 532—535).—$CCl_3{\cdot}CMe{:}CH_2$ (I) is very resistant to attack by Br in CCl_4 or aq. $KMnO_4$ and does not dissolve in conc. H_2SO_4. Addition of HCl or HBr is not practicable because of the ease with which it undergoes the allylic rearrangement. In presence of HF as catalyst, (I) and *p*-OMe·C_6H_4·NH$_2$ smoothly yield *aa-dichloro-γ*-p-*anisyl-β-methyl-*Δ$^{\alpha}$-*propene* (II), b.p. 124—126°/4 mm., oxidised by CrO_3 to *p*-OMe·C_6H_4·CO_2H. $CH_2Cl{\cdot}CMe{:}CCl_2$, formed by allylic rearrangement of (I) under the influence of HF, gives very little (II) when treated with *p*-OMe·C_6H_4·NH_2 and HF under the same conditions. The formation of (II) from (I) may therefore be interpreted as a direct addition of the base to the double linking in (I) in opposition to Markovnikov's rule; the additive product then gives (II) by loss of HCl. It is, however, possible that the dissociation of (I) gives a resonating ion common to both the allylic rearrangement and the Friedel–Crafts reaction. H. W.

Reactions of monovinylacetylene with chlorine and bromine. K. Rengert and H. J. Schumacher (*Ber.*, 1940, **73**, [*B*], 1025—1042).—$CH_2{:}CH{\cdot}C{:}CH$ (I) and Br, when illuminated at 60—150°/100 mm., give a liquid mixture, $C_4H_4Br_4$, b.p. 172—180°/20 mm., the low v.p. of which prevents investigation of the kinetics; the thermal reaction also interferes. Thermal interaction of Cl_2 with (I) is a chain reaction up to 650 mm., leading to a mixture, $C_4H_4Cl_4$, b.p. 90—110°/25 mm., or, if an excess of (I) is used, mainly to a product (II), $C_4H_4Cl_2$, b.p. 35°/40 mm. Investigation of the kinetics is complicated by the stepwise reaction, rearrangement of (II), polymerisation, and addition of Cl_2 to the polymers. H_2 and O_2, if introduced, take part in the reaction. R. S. C.

[Laboratory] preparation of nitroethane. H. McCombie, B. C. Saunders, and F. Wild (*J.C.S.*, 1944, 24—25).—Et_2SO_4 (100 g.) is shaken for 20 hr. with $NaNO_2$ (100 or 150 g.) in H_2O (125 or 187 g.). The best yield is 46% (65% on Et_2SO_4 not recovered), based on Et_2SO_4 → $NaEtSO_4$. More $EtNO_2$ is obtained by distilling solid $NaEtSO_4$, $NaNO_2$, Na_2CO_3, and a little H_2O above 100°. S. A. M.

Reduction of nitroparaffins in liquid ammonia. G. W. Watt and C. M. Knowles (*J. Org. Chem.*, 1943, **8**, 540—543).—$EtNO_2$, Pr$^{\alpha}NO_2$, Pr$^{\beta}NO_2$, Bu$^{\alpha}NO_2$, and Bu$^{\beta}NO_2$ dissolve in and react with liquid NH_3 at −33·5° to form relatively unstable NH_4 salts of the type $CHR{:}N(\rightarrow O){\cdot}ONH_4^+$. All are colourless, cryst. solids which decompose slowly with liberation of NH_3. Qualitatively the decreasing order of stability of the corresponding NH_4 salts is Pr$^{\beta}NO_2$ > Bu$^{\beta}NO_2$ > Pr$^{\alpha}NO_2$ > Bu$^{\alpha}NO_2$ > $EtNO_2$. When Na is added to liquid NH_3 containing a nitroparaffin with an excess of NH_4Br the quantity of H_2 liberated is almost exactly equiv. to that of the Na taken. Removal of the solvent and decomp. of the NH_4 salts results in recovery of the nitroparaffins. Addition of Na to solutions of these nitroparaffins in liquid NH_3 results in the liberation of H_2, the formation of white ppts. (probably of Na salts), and, after addition of NH_4Br, the isolation of the corresponding alkylhydroxylamines, solutions of which readily reduce Ag_2O–NH_3 at room temp. The yields are low owing to slow and incomplete reduction and to the difficulties in separating small quantities of these products from relatively large quantities of inorg. salts. The following must be prepared under anhyd. conditions: p-*nitrobenzaldoxime Et*, m.p. 122—123°, *Pr*$^{\alpha}$, m.p. 77—78°, and *Bu*$^{\beta}$, m.p. 80—81°, *ether*. iso-*Propylhydroxylamine hydrochloride* and n-*butylhydroxylamine platinichloride* are described. M.p. are corr. H. W.

Polymerisation of vinyl ethers. I. Vinyl *n*-butyl ether. M. F. Schostakovski and I. F. Bogdanov (*J. Appl. Chem. Russ.*, 1942, **15**, 249—259).—OBu$^{\alpha}{\cdot}CH{:}CH_2$ (I) prepared (not quite pure) from Bu$^{\alpha}$OH and C_2H_2, b.p. 92—93°, is polymerised by $SnCl_4$ or $FeCl_3$ to an oil (n and η of 1% solutions in C_6H_6 given). The heat of polymerisation is 11·6—14·4 kg.-cal. per 100 g.; to prevent overheating the mixture of monomer and catalyst is either cooled (to keep the temp. at 40—60°) or diluted with polymer. Some η vals. are given for (I)–Bu$^{\alpha}$OH mixtures. J. J. B.

Role of neighbouring groups in replacement reactions. VII. Methoxyl group. S. Winstein and R. B. Henderson (*J. Amer. Chem. Soc.*, 1943, **65**, 2196—2200; cf. A., 1943, II, 228).—Owing to interaction of neighbouring groups, reaction of CHMeBr·CHMe·OMe or *trans*-1-bromo-2-methoxy*cyclo*hexane (I) occurs substantially without inversion. threo-, b.p. 55·6—55·7°/40 mm., and erythro-*β-Bromo-γ-methoxy*-n-*butane*, b.p. 55·7—56·2°/40 mm., are obtained by *trans*-addition to (CHMe:)$_2$ by NHBrAc + H_2SO_4 (trace) in MeOH at < 0°. The following are prepared by known methods: threo-, b.p. 126·4—126·5°/752 mm. (*α-naphthylurethane*, m.p. 84—85°; *acetate*, b.p. 154·8—155·4°/750 mm.), and erythro-*γ-methoxy*-n-*butan-β-ol*, b.p. 132·3—132·5°/748 mm. (*α-naphthylurethane*, m.p. 111—112°; *acetate*, b.p. 153·4—154·0°/749 mm.); *trans*-2-methoxy*cyclo*hexanol (from the oxide by H_2SO_4–MeOH), b.p. 72·5—73·2°/100 mm. (3 : 5-*dinitrobenzoate*, m.p. 101—102°; *acetate*, b.p. 87·5—88·0°/10 mm.). (I) could not be resolved by brucine. R. S. C.

Fructose-1 : 6-diphosphoric acid and fructose-6-monophosphoric acid. C. Neuberg, H. Lustig, and M. A. Rothenburg (*Arch. Biochem.*, 1943, **3**, 33—44).—Ba H_2 *d*-fructose-1 : 6-diphosphate (I) was prepared from the strychnine H salt by treatment with $Ba(OH)_2$,H_2O in MeOH, $[\alpha]_D^{17}$ +4·04° to +4·15° (free acid), reducing power (K salt) 0·48 times that of *d*-fructose, and resistant to Br–H_2O. The Ba H salt was prepared by treating (I) with HBr at 3° and pptn. with EtOH. Partial hydrolysis of fructose-1 : 6-diphosphates (Ca salt with HCl, Ba salt with HBr) at 35° gave 50% yield of Ba *d*-fructose-6-phosphate, $[\alpha]_D^{19}$ +3·58° (Ba salt), reducing power (K salt) 0·82 times that of *d*-fructose, and resistant to Br–H_2O. E. R. S.

Invert soaps. II. Dimethyl-butyl-, octyl-, -dodecyl-, and -hexadecyl-sulphonium iodides. R. Kuhn and O. Dann (*Ber.*, 1940, **73**, [*B*], 1092—1094; cf. A., 1944, II, 115).—RSMe and MeI–N_2 at ~20° give dimethyl-butyl-, *-octyl-*, *-dodecyl-*, and *-hexadecyl-sulphonium iodide*, all cryst. but very hygroscopic. RHal and NaSMe in EtOH at room temp. to −10° (exothermic) and then the b.p. give Me octyl, b.p. 100·5—102·5°/17—18 mm., *dodecyl*, b.p. 163—165°/19 mm., and *hexadecyl sulphide*, m.p. 19·5—20·5°. SMe_2RI is surface-active if R = $C_{>8}$; SMe_2RI are effective against *B. coli* and staphylococci, respectively, at the following concns.: R = Me, Bu, or octyl >2%, $C_{12}H_{25}$ 0·1, 0·2%, and $C_{16}H_{33}$ 0·5, 0·02%; for $C_{12}H_{25}{\cdot}SMeCl{\cdot}CH_2Ph$ the concns. are 0·1 and 0·067, for $C_{12}H_{25}{\cdot}NMe_2Br{\cdot}CH_2Ph$ 0·0167 and 0·02%, respectively. R. S. C.

Methanetri-β-propionic acid.—See A., 1944, III, 33.

Reaction of sodium triphenylmethyl with esters of αβ-unsaturated acids.—See A., 1944, II, 99.

Glycidyl esters of aliphatic acids. E. B. Kester, C. J. Gaiser, and M. E. Lazar (*J. Org. Chem.*, 1943, **8**, 550—556).—*Glycidyl laurate*, b.p. 126°/1 mm., 290° (decomp.)/760 mm., m.p. 21°, *myristate*, b.p. 146°/1 mm., 310° (decomp.)/760 mm., m.p. 33·5—34·5°, *palmitate* (I), b.p. 170°/1 mm., m.p. 44·5—45·0°, *stearate*, b.p. 193°/1 mm., m.p. 50·5—51·3°, and *oleate*, b.p. 185°/1 mm., m.p. −1°, and *β-methylglycidyl myristate*, b.p. 130°/1 mm., m.p. 21·5°, are obtained by boiling the requisite Na salt with epichlorohydrin (II) (or β-methylepichlorohydrin) in excess. The best results are obtained under atm. pressure and strictly anhyd. conditions. The use of increased pressures shortens the time of reaction considerably but the increased temp. favours the formation of quantities of material of high b.p. With imperfectly dried reactants at atm. pressure

50—60% of materials polymerised or of high b.p. are produced. An excess of (**II**) is preferable to PhMe or light petroleum to produce fluidity of the soap suspension. (**II**) does not react satisfactorily with Na sebacate and *glycidyl sebacate*, m.p. 44°, is best obtained from glycidol and sebacyl chloride in PhMe containing NEt_3 as acceptor for HCl in place of C_5H_5N, thus enabling NEt_3,HCl to be almost quantitatively filtered off. (**I**) is obtained similarly The soaps are best obtained by neutralising the fatty acid in $COMe_2$ with 5N-NaOH. Glycidyl esters of the mixed acids of babassu, soya-bean, walnut, and castor oils and rosin have been prepared. H. W.

Synthesis of *d*(−)-β-phosphoglyceric acid and *d*(+)-α-phosphoglyceric acid. C. Neuberg (*Arch. Biochem.*, 1943, **3**, 105—112).—*d*(−)-Glyceric acid was phosphorylated by $EtPO_3$, and the insol. Ba H *d*(−)-β-phosphoglycerate obtained in 70% yield; Ag *d*(+)-α-phosphoglycerate was obtained also in 7% yield. The synthetic and natural products are identical. E. R. S.

Quantitative effect of *X*-rays on ascorbic acid in simple solution and in mixtures of naturally occurring compounds.—See A., 1944, III, 284.

Mechanism of ketol formation from pyruvate and aldehydes. R. L. Berg and W. W. Westerfeld (*J. Biol. Chem.*, 1944, **152**, 113—117).—Oxidation of $(CHMe{\cdot}OH)_2$, CHMeAc·OH, and Ac_2 by KIO_4 leads to rupture of the linking between the substituted C atoms and conversion of the substituent OH groups into CHO while the CO groups are transformed into CO_2H. Oxidation of the 4-C ketol produced in the enzymic reaction between pyruvate (**I**) and EtCHO gives AcOH and EtCHO, thereby identifying the ketol as CHEtAc·OH. Association of CO of the ketol with the 2-C portion of the structure derived from (**I**) makes doubtful the possibility of intermediate compound formation between EtCHO and (**I**) prior to the decarboxylation of the latter. H. W.

Reaction of ethylenediamine with Zeise's salts. A. Gelman (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, **38**, 243—246; cf. A., 1940, I, 267).—$(CH_2{\cdot}NH_2)_2$ (**I**) and aq. Zeise's salt $[K(PtC_2H_4Cl_3)]$ afford a complex, *Pt ethylene ethylenediamine dichloride*, $(C_2H_4{\cdot}PtCl_2{\cdot}NH_2{\cdot}CH_2)_2$ (**II**); no cycle is formed, but (**I**) unites two central atoms as a bridge. Evaporation of the mother-liquor from (**II**) at 100° (bath) gives C_2H_4 and $(CH_2{\cdot}NH_2)_2PtCl_2$. (**I**) and the butadiene salt, $K_2[(PtCl_3)_2C_4H_6]$, afford the very long-chain complex, *Pt butadiene ethylenediamine dichloride* (**III**); the bridges between two central atoms are formed by butadiene on the one hand and (**I**) on the other. (**II**) and (**III**) are decomposed by boiling H_2O. The probable reason why (**I**) does not follow Tschugaev's rule when there is a C_2H_4 mol. in the inner sphere is the instantaneous formation of an insol. ppt. $[(PtCl_2{\cdot}C_2H_4)_2(CH_2{\cdot}NH_2)_2]$, when an attempt is made to introduce (**I**). A. T. P.

Synthesis of amino-acids from substituted cyanoacetic esters. P. E. Gagnon, R. Gaudry, and F. E. King (*J.C.S.*, 1944, 13—15).—Alkylcyanoacetic esters are converted into hydrazides, to which the Curtius reaction is applied (cf. Darapsky, A., 1936, 1494). $CN{\cdot}CHPr^{\beta}{\cdot}CO_2Et$ gives a syrupy hydrazide, which gives 60% yield of valine (PhNCO gives α-N-*phenylcarbamido*isovaleric acid, m.p. 149°). $CN{\cdot}CH_2{\cdot}CO_2Et$ (**I**) and CH_2PhBr give 44% yield of $CH_2Ph{\cdot}CH(CN){\cdot}CO_2Et$, b.p. 165—173°/15 mm. [*hydrazide* (**II**), m.p. 123—124°], and 23% yield of *Et* α-*cyano*-ββ-*dibenzylacetate*, b.p. 190—200°/15 mm. (*hydrazide*, m.p. 235—237°); (**II**) gives 50% yield of phenylalanine (*phenylcarbamyl derivative*, m.p. 168—170°). (**I**) and anisyl chloride give 48% yield of *Et* α-*cyano*-β-*anisylpropionate*, b.p. 165—170°/0·2 mm.; the *hydrazide*, m.p. 122—123°, gives 30% yield of *O*-methyltyrosine, but if conc. HCl–AcOH is used in place of the usual 20% HCl for the final hydrolysis of the urethane, tyrosine is obtained (yield 11%): (**I**) and $OPh{\cdot}[CH_2]_3{\cdot}Br$ give *Et* α-*cyano*-δ-*phenoxyvalerate* (40% yield), b.p. 175—190°/0·7 mm.; the *hydrazide*, m.p. 85°, gives a 40% yield of α-*amino*-δ-*phenoxyvaleric acid*, m.p. 265—267° (decomp.), with which PhNCO forms a *phenylureide*, m.p. 158°. (**I**) and $Br{\cdot}[CH_2]_3{\cdot}CO_2Et$ give 40% yield of Et_2 α-*cyanoadipate*, b.p. 178—186°/15 mm.; the *dihydrazide*, m.p. 128°, cannot be converted into the desired ornithine. Similarly (**I**) and $Br{\cdot}[CH_2]_4{\cdot}CO_2Et$ give 30% yield of Et_2 α-*cyanopimelate*, b.p. 183—197°/12 mm., the *dihydrazide*, m.p. 115—116°, from which cannot be converted into lysine. S. A. M.

Raman spectrum of glycine.—See A., 1944, I, 78.

New mode of formation of β-alanine. C. Enders [with Zellweger] (*Naturwiss.*, 1943, **31**, 209).—A substance promoting the growth of yeast and considered to the β-alanine is obtained when AcCHO is heated with 40% NH_3 at 100°. It is also formed in neutral or slightly acid solution from AcCHO and glycine. The mechanism of the change is discussed. H. W.

Complex compounds of diguanide with bivalent metals. VII.—See A., 1944, I, 89.

Optical antipodes of pantothenic acid. R. Kuhn and T. Wieland (*Ber.*, 1940, **73**, [*B*], 1134).—Resolution of *dl*-pantothenic acid by quinine in $COMe_2$–EtOH or COMeEt gives *d*- and *l*-acids, $[\alpha]_D^{20}$ ±27° in H_2O. The *d*-acid has 45—50 × 10^6 SbmE units of activity per g.; the *l*-acid is inactive (cf. A., 1942, II, 297; 1944, II, 36). R. S. C.

Analogues of pantothenic acid. III. Preparation of growth-inhibiting analogues related to *N*-pantoyltaurine (Miss) J. Barnett (*J.C.S.*, 1944, 5—8; cf. A., 1942, II, 250; III, 621).—$NH_2{\cdot}[CH_2]_2{\cdot}SH$ [from $(CH_2)_2NH$ and H_2S](2 : 4-*dinitrobenzoylthioether*, m.p. 93·5—94·5°) and pantolactone (α-hydroxy-ββ-dimethylbutyrolactone) (**I**) in a sealed tube in vac. (100°, 1 hr.) give *N-pantoyl*-β-*aminoethylthiol* (**II**), a yellow oil (86% pure), highly toxic to rats. $(NH_2{\cdot}[CH_2]_2)_2S_2$ and (**I**) in abs. MeOH (reflux, 1 hr.) give *bis*-(*N-pantoyl*-β-*aminoethyl*) *disulphide* (**III**), m.p. 141—144°. $(NH_2{\cdot}[CH_2]_2)_2S$ (**IV**) and (**I**) in abs. MeOH (cold, 12 hr.; reflux, 1 hr.) give *bis*-(*N-pantoyl*-β-*aminoethyl*) *sulphide* (**V**), a viscous oil. (**IV**) and Br–H_2O give *bis*-β-*aminoethyl sulphoxide dihydrobromide*, m.p. 201—202° (quant. yield, ~100% pure); this with NaOEt gives the *sulphoxide* (**VI**), a syrup [*dihydrochloride* (**VII**), m.p. 220°; 97% pure]. (**VI**) and (**I**) in abs. MeOH (20°, 3 days) give *bis*-(*N-pantoyl*-β-*aminoethyl*) *sulphoxide* (**VIII**), a syrup (~92% pure); after 3 months in a sealed tube. $COMe_2$ extracts a compound, m.p. 143—144°, identical with (**III**). (**IV**) or (**VII**) and $KMnO_4$ in 50% AcOH give 50% yield of *bis*-β-*aminoethyl sulphone dihydrochloride*, m.p. 226—228°; the sulphone and (**I**) in abs. MeOH (reflux, 1 hr.) give *bis*-(*N-pantoyl*-β-*aminoethyl*) *sulphone* (**IX**), a syrup. (**II**) and (**III**) inhibit the growth *in vitro* of *Lactobacillus arabinosus* to approx. the same degree as pantoyltaurine, (**V**), (**VIII**), and (**IX**) to a smaller degree; rats are more susceptible to *Streptococcus hæmolyticus* in presence of any of these substances than in their absence. S. A. M.

Dimethanesulphonimide, a strong acid. B. Helferich and H. Grünert (*Ber.*, 1940, **73**, [*B*], 1131—1133).—$NH(SO_2Me)_2$ is best (~90%) obtained by adding 5N-NaOH (4) and $MeSO_2Cl$ (2 mols.) to conc., aq. NH_4Cl (1 mol.) at 0°. It is a strong acid (cf. A., 1942, II, 297); 0·1, 0·01, and 0·001N. solutions have pH 1·27, 2·20, and 3·25, respectively. With $CHMeN_2$ it gives *dimethanesulphonethylimide* (100%), m.p. 94—95° (corr.), also obtained (47%) from NH_2Et,HCl (1 mol.), $MeSO_2Cl$ (2·6), and NaOH (4·7 mols.) at 0—5°. NH_2R,HCl (1), $MeSO_2Cl$ (1 mol.), and NaOH (2—2·21 mols.) at 2—5° give *methanesulphon-ethylamide*, b.p. 105·5—107° (corr.)/0·3 mm., and *-methylamide* (~60%), b.p. 118°/0·3 mm. [with some *dimethanesulphonmethylimide*, m.p. 115·5—116·5° (corr.)]. R. S. C.

Trimethylacetic acid. Isolation and degradation of pivalazide. A. Buhler and H. E. Fierz-David (*Helv. Chim. Acta*, 1943, **26**, 2123—2136).—The behaviour of *pivalazide* (**I**) contradicts the theory that an enolisable CO or a vicinal C:C linking is essential for the Curtius transformation of azides. Survey of the literature leads to the conclusion that at present there is no experimentally established theory of the isomerisation incident to the Hofmann and Curtius degradations. Freshly sublimed pivaloylhydrazine, m.p. 56—57°, in 2N-HCl at −5° to −3° is converted by $NaNO_2$ into (**I**), a mobile, odourless liquid, m.p. 0°, which can (generally) be distilled unchanged in a high vac.; it is less advantageously prepared from $Bu^{\gamma}COCl$ and NaN_3. It passes quantitatively at 100° into N_2 and $Bu^{\gamma}NCO$, b.p. 84·6° (corr.), a colourless liquid with a pleasant odour, which does not solidify at −30° and could not be polymerised by prolonged irradiation. The following are described: NN′-*di*tert.-*butyl*-, m.p. 242°, N-*phenyl*-N′-tert.-*butyl*-, m.p. 153° (corr.), and *N-tert.*-butyl-*carbamide*, m.p. 242°; $NHBu^{\gamma}{\cdot}CO_2Me$, b.p. 56°/11 mm., $NHBu^{\gamma}{\cdot}CO_2Et$, b.p. 74°/11 mm., m.p. 30—21°, NH_2Bu^{γ}, b.p. 44° (hydrochloride, m.p. 273—275°). H. W.

Modern methods of preparative organic chemistry. X. Syntheses with diazomethane. B. Eistert (*Angew. Chem.*, 1941, **54**, 99—105, 124—131).—A review.

II.—SUGARS AND GLUCOSIDES.

Methanesulphonates of the sugar group. III. B. Helferich and H. Jochinke (*Ber.*, 1940, **73**, [*B*], 1049—1052; cf. A., 1939, II, 468).—β-Di*iso*propylidenefructose and $MeSO_2Cl$ in C_5H_5N at 0° give 2 : 3-4 : 5-di*iso*propylidene-*d*-fructopyranose 1-methanesulphonate (85%), m.p. 125—126°, $[\alpha]_D^{21}$ −29·3° in $CHCl_3$, converted by H_2SO_4–MeOH–H_2O into syrupy fructose 1-methanesulphonate. Di*iso*propylidenesorbose gives similarly 2 : 3-4 : 6-di*iso*propylidene-l-*sorbofuranose* 1-*methanesulphonate* (~70%), m.p. 116—117°. α-Di*iso*propylidenefructose gives 1 : 2-4 : 5-di*iso*propylidene-d-*fructopyranose* 3-*methanesulphonate* (>90%), m.p. 104—105°, $[\alpha]_D$ −161·4° in $CHCl_3$, converted by boiling H_2SO_4–MeOH–H_2O into syrupy *d*-fructose 3-methanesulphonate or, by shorter treatment, into 1 : 2-iso*propylidene*-d-*fructopyranose* 3-*methanesulphonate* (**I**) (variable yield up to 70%), m.p. 133° (decomp.), $[\alpha]_D$ −138° in $COMe_2$. With $MeSO_2Cl$–C_5H_5N at 0°, (**I**) gives 1 : 2-iso*propylidene*-d-*fructopyranose* 3 : 4 : 5-*trimethanesulphonate*, m.p. 128—130°, $[\alpha]_D$ −115·5° in $CHCl_3$, or with Ac_2O–C_5H_5N at 37° gives 1 : 2-iso*propylidene*-d-*fructopyranose* 4 : 5-*diacetate* 3-*methanesulphonate* (>90%), m.p. 84—86°. Phenyl-β-*d*-fructopyranoside with $MeSO_2Cl$–C_5H_5N at 0° gives *phenyl*-β-d-*fructopyranose tetramethanesulphonate* (>85%), m.p. 197° (decomp.), $[\alpha]_D$ −135·3° in C_5H_5N, or at −19° gives, after

acetylation, impure *phenyl-β-*d-*fructopyranoside triacetate* 1-*methanesulphonate* (II), whence boiling NaOMe–MeOH gives *phenyl-β-fructopyranoside* 1-*methanesulphonate*, m.p. 120° (decomp.), $[\alpha]_D$ −172·2° in C_5H_5N, which by reacetylation gives pure (II), m.p. 127—128°, $[\alpha]_D^{19}$ −135·4° (does not react with NaI–$COMe_2$ at 125—130°). R. S. C.

Splitting of sucrose by ultrasound.—See A., 1944, I, 88.

Starch. XI. Highly methylated starch. Sugars obtained by fission. XII. Comparison of end-group content, viscosity, and osmotic pressure of starch and its components. K. Hess and E. Steurer (*Ber.*, 1940, **73**, [*B*], 1069—1076, 1076—1079).—XI. When methylated potato starch (40—41% OMe) is treated with Na, liquid NH_3, and MeI in PhOMe, the product contains usually ~44—45·5% of OMe; high OMe content is obtained only if not too much Na is used, an excess causing back-hydrolysis. MeI–Ag_2O similarly gives variable results up to 45·6% of OMe. Hydrolysis of a product containing 45·55% of OMe gives methyl-tetra- 3·99, -tri- 86·7, -di- 4·77, and -mono-methylglucoside 2·27%. It is concluded that methylation is still incomplete but may involve structural changes.

XII. Data on the end-group content, η, and osmotic pressure of starch (potato; maize) and amylo- and erythro-amylose are recorded. They are considered too inconsistent to serve as a basis for final generalisation. R. S. C.

Limit dextrins and starch. XII. Preparation and constitution of a difficultly hydrolysable disaccharide ("*iso*maltose") from starch. K. Ahlborg and K. Myrback (*Biochem. Z.*, 1941, **308**, 187—195; cf. A., 1944, II, 8; III, 67).—The prep. of *iso*maltose (I) from maize starch by hydrolysis with 0·2N-H_2SO_4 followed by removal of glucose and fractional pptn. with EtOH is described. Hydrolysis of a limit dextrin with takadiastase gives 20% yield of (I). The theoretical yield is calc. to be ~36%, whence it is concluded that the mol. of the limit dextrin with mol. wt. 700—1000 contains one (I) unit. The action of pancreatin on potato starch shows that it contains one (I) for every 15—20 maltose units. Since amylose is probably not branched, amylopectin must contain one (I) to every 10 maltose units. The structure of (I) is shown by methylation followed by hydrolysis, which yields 2 : 3 : 4-tri- and 2 : 3 : 4 : 6-tetra-methylglucose. J. N. A.

Phosphorylase of waxy maize.—See A., 1944, III, 289.

Amorphin, a glycoside in *Amorpha fruticosa*, L. F. Acree, jun., M. Jacobson, and H. L. Haller (*J. Org. Chem.*, 1943, **8**, 572—574).—The seeds of *A. fruticosa*, L., give the colour reaction in the Durham test which heretofore has been considered sp. for rotenone and the rotenoids, but no compounds of this class could be isolated from them. The product responsible for the positive reaction is *amorphigenin* (I), $C_{22}H_{22}O_7$, the aglycon of the glycoside, amorphin (II), $C_{33}H_{40}O_{16}$. (I) has m.p. 191—192°, does not reduce Fehling's solution before or after acid hydrolysis, and gives a negative phenol test. (II) has m.p. 151—151·5°, does not reduce Fehling's solution until after acid hydrolysis, and gives a positive Durham and orcinol test and a negative phenol test. A substance, m.p. 218°, which gives a positive Durham test has been isolated in quantity too small for extended examination. H. W.

III.—HOMOCYCLIC.

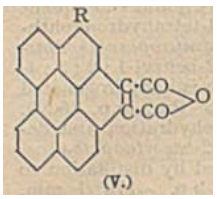
Action of ultra-violet light on liquid benzene. C. B. Allsopp and B. Szigeti (*J.S.C.I.*, 1944, **63**, 31—32).—When liquid C_6H_6 is irradiated in presence of air with ultra-violet light of λ 2537 A., small quantities of five different substances can be separated by chromotographic fractionation of the products. The absorption spectrum of one of them resembles those of the diphenylpolyenes, and another yields a bromophenylhydrazone. None of them has been definitely identified.

2 : 3 : 5-Trimethylnaphthalene in coal tar. O. Kruber (*Ber.*, 1940, **73**, [*B*], 1174—1175).—The first cryst. sulphonic acids obtained by partial sulphonation (with 92% H_2SO_4) of a neutral, heavy oil fraction, b.p. 286—289°, readily yield 2 : 3 : 5-*trimethylnaphthalene* (I), b.p. 285°/762 mm., m.p. 25·3° (picrate, m.p. 124°; styphnate, m.p. 148°), after purification through the K salts. The hydrocarbon from subsequent sulphonates requires purification through the picrate, which is successful only if much preliminary enrichment has been effected by sulphonation. Its constitution is established by its oxidation by CrO_3 in AcOH at 60° to 2 : 3 : 5-*trimethyl*-1 : 4-*naphthaquinone*, m.p. 128°, which is further oxidised by aq $KMnO_4$ at 60—70° to 3 : 1 : 2-$C_6H_3Me(CO_2H)_2$, m.p. 154°, or to 2 : 3 : 1-$C_6H_3Me_2{\cdot}CO_2H$ if excess of $KMnO_4$ is used at 100°. H. W.

Syntheses in the naphthalene group. III. Syntheses of 2-benzylnaphthalenes. W. Borsche, P. Hofmann, and H. Kuhn [and, in part, R. Manteuffel] (*Annalen*, 1943, **554**, 23—40; cf. A., 1937, II, 18, 257).—α-Phenacylcinnamic acid (I) is hydrogenated (Pd–C in EtOAc) to *α-phenacyl-β-phenylpropionic acid*, reduced (Zn–Hg and HCl in boiling MeOH) followed by hydrolysis to γ-phenyl-α-benzyl-*n*-butyric acid, b.p. 198°/1 mm., m.p. 54—55°, also obtained by hydrogenation (Pd–C in EtOAc) of (I) or of phenylbenzylcrotonolactone. This is converted by treatment with PCl_3 and subsequent distillation in vac. into 1-keto-2-benzyl-1 : 2 : 3 : 4-tetrahydronaphthalene (II), b.p. 176°/1 mm., m.p. 53—54° (2 : 4-*dinitrophenylhydrazone*, m.p. 53—54°), reduced (Clemmensen) to 2-benzyl-1 : 2 : 3 : 4-tetrahydronaphthalene, b.p. 195°/13 mm., which is dehydrogenated by Se at 280—300° to 2-$C_{10}H_7{\cdot}CH_2Ph$, m.p. 58° (lit., m.p. 35·5°). (II) is transformed by MgPhBr followed by dehydration and dehydrogenation (Se) of the product into 1-*phenyl*-2-*benzylnaphthalene*, m.p. 87—88°. $(CH_2Ph)_2CH{\cdot}CH_2{\cdot}COCl$ is cyclised by distillation to 1-*keto*-3-*benzyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b.p. ~170°/1 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 220°), which is reduced and dehydrogenated to (III), m.p. 57—58°. 2-$C_{10}H_7{\cdot}COPh$ is reduced by N_2H_4,H_2O at 220—230° to 2-$C_{10}H_7{\cdot}CH_2Ph$, m.p. 58° (picrate, m.p. 93°). 1-$C_{10}H_7{\cdot}COPh$ is transformed similarly into 1-$C_{10}H_7{\cdot}CH_2Ph$, m.p. 57·5—58° (picrate, m.p. 103—104°). Na β-anisoylpropionate, PhCHO, and Ac_2O at 100° afford p-*anisylbenzylidenecrotonolactone*, m.p. 176—177°, converted by Na_2CO_3 in boiling aq. MeOH into α-p-*methoxyphenacylcinnamic acid*, m.p. 171°, which is hydrogenated to α-p-*methoxyphenacyl-β-phenylpropionic acid*, m.p. 132°; this is reduced (Clemmensen) to *α-benzyl-γ-*p-*anisyl*-n-*butyric acid*, b.p. ~200°/1 mm., m.p. 77°, which is cyclised to 1-*keto*-7-*methoxy*-2-*benzyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (III), b.p. 202—204°/1 mm., m.p. 120—121° (2 : 4-*dinitrophenylhydrazone*, m.p. 223°). Reduction (Clemmensen) followed by dehydrogenation (Se) of (III) leads to 7-*methoxy*-2-*benzylnaphthalene*, m.p. 75·5° (*picrate*, m.p. 92—93°). γ-p-*Anisylbutyric acid*, m.p. 53—55°, is smoothly obtained by hydrogenation (Pd–C in EtOAc) of γ-keto-γ-*p*-anisyl-*n*-butyric acid. *γ-Keto-γ-phenyl-γ-anisylidenebutyric acid*, m.p. 179°, is reduced catalytically and subsequently according to Clemmensen to *γ-phenyl-α-4-methoxybenzylbutyric acid*, m.p. 87°; this gives successively 1-*keto*-2-4′-*methoxybenzyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 65° (2 : 4-*dinitrophenylhydrazone*, m.p. 195°), and 2-4′-*methoxybenzyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 69°, but the subsequent dehydrogenation does not appear to proceed smoothly. Reduction of 2-anisoylnaphthalene by N_2H_4 affords 2-4′-*hydroxybenzylnaphthalene*, m.p. 98° (*picrate*, m.p. 125—126°). Na β-anisoylpropionate, *p*-OMe·C_6H_4·CHO, and Ac_2O at 100° afford p-*anisyl-anisylidene-crotonolactone*, m.p. 175—176°, converted by prolonged boiling with Na_2CO_3 in aq. MeOH into p-*methoxy-α-4-methoxyphenacylcinnamic acid*, m.p. 191°, which is reduced directly to γ-p-*anisyl-α-4-methoxybenzyl*-n-*butyric acid*, m.p. 112°; this is treated with PCl_3 and then cyclised to 1-*keto*-7-*methoxy*-2-4′-*methoxybenzyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b.p. 233—236°/1 mm., m.p. 90·5° (2 : 4-dinitrophenylhydrazone, m.p. 200°), which is reduced (Clemmensen) and then dehydrogenated (Se at 280—300°) to 7-*methoxy*-2-4′-*methoxybenzylnaphthalene*, m.p. 121·5°. Na β-veratroylpropionate, PhCHO, and Ac_2O at 100° give 3 : 4-*dimethoxyphenylbenzylidenecrotonolactone* (IV), m.p. 139—140°, converted by Na_2CO_3 in boiling aq. MeOH into α-3 : 4-*dimethoxyphenacylcinnamic acid*, m.p. 212°, and by boiling NaOMe–MeOH with immediate acidification into *Me* α-3 : 4-*dimethoxyphenacylcinnamate*, m.p. 121—122°, which is transformed by N_2H_4,H_2O at 120—130° into 3-*keto*-6-3′ : 4′-*dimethoxyphenyl*-4-*benzyl*-2 : 3 : 4 : 5-*tetrahydropyridazine*, m.p. 173—174°. The ester is hydrogenated to *Me* α-3 : 4-*dimethoxyphenacyl-β-phenylpropionate*, m.p. 136—137° (corresponding *acid*, m.p. 140°), which is reduced (Clemmensen) to γ-3 : 4-*dimethoxyphenyl-α-benzylbutyric acid*, b.p. ~240°/1 mm., also obtained by catalytic hydrogenation of (IV) and converted into 1-*keto*-6 : 7-*dimethoxy*-2-*benzyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 143° (2 : 4-*dinitrophenylhydrazone*, m.p. 227°). Gradual addition of NaOMe in MeOH to Me β-veratroylpropionate and PhCHO in MeOH at 30° leads to *β-veratroyl-β-benzylidenepropionic acid*, m.p. 124—126°; this is hydrogenated (Pd–C) in EtOAc) to the corresponding saturated acid, which is reduced (Clemmensen) to the non-cryst. γ-3 : 4-*dimethoxyphenyl-β-benzyl*-n-*butyric acid*, b.p. ~220°/1 mm. The corresponding non-cryst. 1-*keto*-6 : 7-*dimethoxy*-3-*benzyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (2 : 4-*dinitrophenylhydrazone*, m.p. 239°) is dehydrogenated to 6 : 7-*dimethoxy*-2-*benzylnaphthalene*, m.p. 105—106°, which does not give a colour with $FeCl_3$. H. W.

Perylene and its derivatives. LI. A. Zinke, U. Noculak, R. Skrabal, and H. Troger (*Ber.*, 1940, **73**, [*B*], 1187—1192).—Gradual addition of Br to a solution of perylene in boiling C_6H_6 gives a *tetrabromoperylene* (I), m.p. 310°, which gives a dark green colour in conc. H_2SO_4 and a more freely sol. (probably non-homogeneous) tetrabromoperylene (II), m.p. (indef.) 198—203°, which dissolves in warm conc. H_2SO_4 to a blue solution becoming violet and then dirty red when further heated. Under similar conditions 3 : 9-dibromoperylene gives (I) and a further tetrabromoperylene (III), m.p. 250—251°, whereas the 3 : 10-Br_2-compound gives a tetrabromoperylene (IV), m.p. 265°, softens at 254°. It is uncertain whether (II), (III), and (IV) are isomeric compounds or identical products in different stages of purity. Hot conc. H_2SO_4 transforms (I), (II), (III), and (IV) into quinones which are non-cryst. and sol. in alkali. (I) and conc. H_2SO_4 at 90° give a *product* with the approx. composition of a dibromoperylenequinone. Attempts to establish the position of Br in (I), (II), (III), and (IV) by use of $(CH{\cdot}CO)_2O$ are shown to be useless since no reaction occurs with

3 : 4 : 9 : 10-tetra-chloro- or -nitro-perylene although the 1 : 12-positions are free. Condensation with $(CH{\cdot}CO)_2O$ is not completely inhibited by the presence of substituents since 3 : 9-dichloroperylene gives a *compound* [(V), R = Cl] and 3 : 9-dibenzoylperylene affords a *substance* [(V), R = Bz]. Treatment of this with $AlCl_3$ at 170—180° gives varying results; it is decarboxylated by NaOH–CaO to 1 : 12-benzperylene, m.p. 272°, the Bz groups being removed. Decarboxylation of 4 : 5-*benz*-1 : 2-*diphenylaceperylene*-Bz1 : Bz2-*dicarboxylic anhydride* leads to a *hydrocarbon*, m.p. 279°, with the composition of the expected diphenylacebenzperylene but it is doubtful whether both Ph groups are still present. Condensation of tribenzoylperylene with $(CH{\cdot}CO)_2O$ in boiling $PhNO_2$ yields *tribenzoyl*-1 : 12-*benzperylene*-Bz1 : Bz2-*dicarboxylic anhydride*.



(V.)

Invert soaps. III. Benzylmethyldialkylammonium chlorides. R. Kuhn, D. Jerchel, and O. Westphal (*Ber.*, 1940, **73**, [*B*], 1095—1100; cf. A., 1944, II, 90).—CH_2PhCl and $NMeR_2$ at 110—120° give *benzylmethyldi-butyl*-, m.p. 181°, *-hexyl*-, m.p. 58°, *-octyl*- (I), m.p. 68°, *-dodecyl*- (II) (prep. in EtOH at 120° and then 90°), m.p. 96°, and *-cetyl-ammonium chloride* (III) (prep. in EtOH at 100°), m.p. 99°. *Dimethyldi-hexyl*-: m.p. ~35°, and *-tetradecyl-ammonium methosulphate*, m.p. 129—130°, and *methylethyldidodecylammonium iodide*, m.p. 149°, and nitrate, m.p. 14°, are also prepared. Surface activity reaches a sharp max. at (II). For $CH_2Ph{\cdot}NMeR_2Cl$, efficiency against *Streptobacterium plantarum* is a max. with (II). Efficiency against staphylococci, *B. coli*, *E. typhi*, and Friedländer bacillus is a max. at (I); against paratyphoid-*B* bacteria, (II) is as effective as (I). R. S. C.

Aniline homologues in coal tar. O. Kruber and L. Rappen (*Ber.*, 1940, **73**, [*B*], 1178—1184).—The most volatile fractions obtained in the separation of quinoline (I) are acetylated and the Ac derivatives are separated from one another by fractional crystallisation. The total primary bases constitute only 0·12% of crude (I). The presence of *o*-, *m*-, and *p*-toluidine, *m*-4-, *p*-, *m*-5- (II), and *o*-3-xylidine is established. The three toluidines are present in tar in about the same ratio as the three cresols. Among the xylidines as among the xylenols the *m*-compounds, particularly (II), predominate. H. W.

Reactions of 3-nitro-1-naphthylamine, including anil formation, bromination, and the preparation of 1 : 2 : 3 : 4-tetrabromonaphthalene. H. H. Hodgson and D. E. Hathway (*J.C.S.*, 1944, 21—22).—3 : 1-$NO_2{\cdot}C_{10}H_6{\cdot}NH_2$ (I) [*Bz*, m.p. 220°, p-*toluenesulphonyl*, m.p. 200°, *CHPh*:, m.p. 122°, o-, m.p. 194°, m-, m.p. 188°, and p-*nitrobenzylidene*, m.p. 242° (sinters at 235°), and p-*hydroxybenzylidene* derivative, m.p. 233°] and Zn–Ac_2O–NaOAc give 1 : 3-$C_{10}H_6(NHAc)_2$, m.p. 264°. (I)–$NaNO_2$–AcOH–H_2SO_4, followed by Cu_2O–EtOH, afford an almost quant. yield of 2-$C_{10}H_7{\cdot}NO_2$. Br (1 or 2 mols.)–$CHCl_3$ converts (I) into 2 : 4-*dibromo*-3-*nitro*-1-*naphthylamine*, m.p. 182° (*Ac* derivative, m.p. 202°). 3 : 2 : 4 : 1-$NO_2{\cdot}C_{10}H_4Br_2{\cdot}N_2HSO_4$ and Cu_2O–EtOH yield 1 : 3-*dibromo*-2-*nitronaphthalene*, m.p. 130·5°; CuBr–HBr (*d* 1·7) at <20° affords 1 : 3 : 4-*tribromo*-2-*nitronaphthalene*, m.p. 218° (reduced by aq. $Na_2S_2O_4$–EtOH to the corresponding *amine*, m.p. 163°), and CuCl–HCl (*d* 1·16) gives 4-*chloro*-1 : 3-*dibromo*-2-*nitronaphthalene*, m.p. 198° (*amine*, m.p. 161°). 1 : 2 : 3 : 4-*Tetrabromonaphthalene*, m.p. 196°, is obtained from 1 : 3 : 4 : 2-$C_{10}H_4Br_3{\cdot}N_2HSO_4$. A. T. P.

Chromophoric naphthalene nucleus.—See A., 1944, I, 52.

"Carpasemine" isolated from *Carica papaya* seeds. T. B. Panse and A. S. Paranjpe (*Proc. Indian Acad. Sci.*, 1943, **18**, **A**, 140—144).—"Carpasemine" (I) (A., 1941, II, 381) is identified as benzylthiocarbamide, m.p. 165° (Ac derivative, m.p. 131°; *methiodide*, m.p. 103—105°). (I) is transformed by boiling 20% NaOH into NH_3, $CH_2Ph{\cdot}NH_2$ (hydrochloride, m.p. 245—246°), and $NH_2{\cdot}CO{\cdot}NH{\cdot}CH_2Ph$, m.p. 148—149° (*Ac* derivative, m.p. 130°), oxidised ($KMnO_4$) to an unidentified *compound*, m.p. 205—207°. A synthesis of (I) starting from $CH_2Ph{\cdot}CN$ is recorded. H. W.

Complex compounds of diguanide with bi- and ter-valent metals. VI. Copper, nickel, and cobaltic phenyldiguanide-*p*-sulphonic acid. P. Ray and S. K. Siddhanta (*J. Indian Chem. Soc.*, 1943, **20**, 250—252; cf. A., 1942, II, 254).—Dicyanodiamide and boiling aq. *p*-$NH_2{\cdot}C_6H_4{\cdot}SO_3H$ give *phenyldiguanide*-p-*sulphonic acid* (I), *p*-$^-SO_3{\cdot}C_6H_4{\cdot}NH{\cdot}C(:NH){\cdot}NH{\cdot}C(:NH){\cdot}NH_3^+$, m.p. 265—268° (decomp.), which behaves as an ampholyte. Aq. $CuSO_4,5H_2O$ (at 50—60°) or $NiCl_2,6H_2O$ (at 100°) added to (I) in an excess of aq. NH_3 affords the *Cu*$^{\cdot\cdot}$, $+H_2O$, or *Ni*$^{\cdot\cdot}$ complex, $+2H_2O$ (probably *trans*-forms). $CoCl_2,6H_2O$ and aeration yields the *Co*$^{\cdot\cdot\cdot}$ complex, $+5H_2O$. A. T. P.

Derivatives of diphenylsulphonamides. I. Preparation of 2-aminodiphenyl-4-sulphonamide. A. H. Popkin. **II. Derivatives of 2'-aminodiphenyl-4-sulphonamide.** A. H. Popkin and (Miss) G. M. Perretta (*J. Amer. Chem. Soc.*, 1943, **65**, 2043—2045, 2046—2048).—I. Adding *o*-$C_6H_4Ph{\cdot}NHAc$ (I) to $ClSO_3H$ at <10° and then heating at 60° gives 2'-*acetamidodiphenyl*-4-*sulphonyl chloride* (II), m.p. 149—150·5°, converted by hot, conc., aq. NH_3 into the *amide*, m.p. 201—202°, which with hot, conc., aq. HCl–MeOH gives 2'-*aminodiphenyl*-4-*sulphonamide* (III), m.p. 186—187°. *o*-$C_6H_4Ph{\cdot}NO_2$ and $ClSO_3H$ give, as above, 2'-*nitrodiphenyl*-4-*sulphonyl chloride* (IV), m.p. 78—80°, and thence the *amide*, m.p. 203—204°, which with Sn–conc. HCl–EtOH yields (III). 2'-*Aminodiphenyl*-4-*sulphonic acid*, decomp. >250°, is obtained from (II) by boiling 18% aq. HCl or from (I) by 96% H_2SO_4 at 120°; when it is diazotised in 10% H_2SO_4 at room temp. and then heated at 60° and the Na_2 salt resulting is fused with NaOH at 270—290°, *o*-$OH{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}OH$-*p*, m.p. 161·5—162·5° [diacetate, m.p. 94·5—96·5° (lit. 94°)], is obtained, thus proving the structure.

II. (II) is unstable when kept. NH_2R and (II) or (IV) in C_5H_5N–$COMe_2$ at 50° and then room temp. give *o*-$NHAc{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}SO_2{\cdot}NHR$-*p* or *o*-$NO_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NHR$-*p*, respectively, converted by HCl–MeOH or Sn–conc. HCl–MeOH respectively into *o*-$NH_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}SO_2{\cdot}NHR$-*p*, which are inactive against *E. coli in vitro* and streptococci in mice. The following are described: 2'-*aminodiphenyl*-4-*sulphon-anilide*, m.p. 100—100·5° (*Ac* derivative, m.p. 163·5—164·5°), *-benzylamide*, m.p. 106·5—107° (*Ac* derivative, m.p. 161—162°), -o-, m.p. 165—165·5° (*Ac* derivative, m.p. 173·5—175°), and -p-*xenylamide*, m.p. 169—170° (*Ac* derivative, m.p. 196—196·5°); 2'-*nitrodiphenyl*-4-*sulphon-anilide*, m.p. 155·5—156·5°, *-benzylamide*, m.p. 128·5—130°, -o-, m.p. 161—162°, and -p-*xenylamide*, m.p. 164—165°; N^4-2''-*acetamido*-, m.p. 231·5—232·5°, N^4-2''-*amino*-, m.p. 197·2—198·2°, and N^4-2''-*nitro-diphenyl*-4'-*sulphonylsulphanilamide*, m.p. 239·5—240°; 2'-2'''-*acetamido*-, m.p. 148·5—150° (decomp.), 2'-2'''-*amino*-, m.p. 263—264°, and 2'-2'''-*nitro-diphenyl*-4''-*sulphonamidodiphenyl*-4-*sulphonamide*, m.p. 173—174°. R. S. C.

Decomposition of the diazonium salts of 4-nitro-1-naphthylamine by sodium sulphite and sodium acetate. Preparation of 4 : 4'-dinitro-1 : 1'-azonaphthalene. H. H. Hodgson, D. E. Nicholson, and G. Turner [with, in part, J. Habeshaw] (*J.C.S.*, 1944, 15—17).—Rapid addition of aq. Na_2SO_3 to 4 : 1-$NO_2{\cdot}C_{10}H_6{\cdot}N_2Cl$ (or $\cdot N_2HSO_4$) (I) + NaOAc (excess) at 0° yields 4 : 4'-*dinitro*-1 : 1'-*azonaphthalene* (II), m.p. 334°, and a trace of 4 : 1-$NO_2{\cdot}C_{10}H_6{\cdot}OH$. Excess of NaOAc alone initiates an oxidation–reduction reaction with (I) and affords (II), 4 : 4'-dinitro-1 : 1'-dinaphthyl (III), m.p. 246°, and (by a simultaneous decomp. by H_2O or OH^-) some 4 : 4'-*dinitronaphthalene*-1' : 2-*azo*-1-*naphthol* (IV), m.p. 278° (also obtained from 4 : 1-$NO_2{\cdot}C_{10}H_6{\cdot}N_2Cl$ and 4 : 1-$NO_2{\cdot}C_{10}H_6{\cdot}OH$ in aq. $NaHCO_3$). (I) and aq. Na_2SO_3 at 0° afford numerous substances, including (II) (10—20%), (III), and 1-$C_{10}H_7{\cdot}NO_2$; no (IV) is formed. In the above reactions, 4 : 4'-*dinitronaphthalene*-1' : 2-*azo*-1-*naphthylamine*, m.p. 274°, is not obtained, but is prepared from 4 : 1-$NO_2{\cdot}C_{10}H_6{\cdot}N_2Cl$ and 4 : 1-$NO_2{\cdot}C_{10}H_6{\cdot}NH_2$ in AcOH–NaOAc. Mechanisms of reactions are postulated, and colour reactions recorded. (II) gives a bright blue colour with H_2SO_4, suggesting that salt formation has produced a di-indamine-like structure. A. T. P.

Replacement of the diazonium by the nitro-group. General method based on decomposition of the aryldiazonium cobaltinitrites. H. H. Hodgson and E. Marsden (*J.C.S.*, 1944, 22—24).—Aryldiazonium *cobaltinitrites* (I), $(ArN_2)_3Co(NO_2)_6$, are prepared by adding $Na_3Co(NO_2)_6$ to a solution of ArN_2Cl neutralised with $CaCO_3$. They decompose on heating, sometimes with explosive violence, and couple with alkaline β-$C_{10}H_7{\cdot}OH$. (I) (Ar = Ph, *o*-, *m*-, and *p*-$NO_2{\cdot}C_6H_4$·, and *p*-C_6H_4Cl·) with Cu_2O in conc. aq. $NaNO_2$ give $PhNO_2$ (75·5%), *o*- (67·4%), *m*- (72%), and *p*-$C_6H_4(NO_2)_2$ (75%), and *p*-$C_6H_4Cl{\cdot}NO_2$ (82·5%), respectively. Small amounts of 1- (20%) and 2-$C_{10}H_7{\cdot}NO_2$ (16·9%) are obtained similarly from (I) (Ar = 1- and 2-$C_{10}H_7$), but $CuSO_4$–Cu_2O–$NaNO_2$ gives 68 and 60%, respectively. Using the latter method, *o*- and *p*-toluidine and *o*- and *p*-anisidine also give >60% of the respective NO_2-compounds. A. T. P.

Interpretation of the Sandmeyer reaction. IV. Catalysed decomposition of diazonium cations by anionoid complexes with special reference to those of cobalt and ferric iron. H. H. Hodgson, S. Birtwell, and J. Walker (*J.C.S.*, 1944, 18—19; cf. A., 1943, II, 28).—% Yields of *m*- and *p*-$C_6H_4Cl{\cdot}NO_2$ (I) obtained by decomp. of *m*- and *p*-$NO_2{\cdot}C_6H_4{\cdot}N_2Cl$ with metallic salts in boiling HCl (*d* 1·16) are recorded in parentheses: HCl alone (47·3; 54·4), hydrated $AlCl_3$ (54·4; 60·7), $SbCl_3$ (31·6; 37·1), anhyd. $CaCl_2$ (47·3; 54·4) hydrated $CoCl_2$ (60·7; 70·9), CuCl, hydrated $CuCl_2$, or anhyd. $FeCl_3$ (67·5; 77·6), anhyd. $ZnCl_2$ (47·3; 54·4); the use of $CrCl_3$, $SnCl_4$, $NiCl_2$, and $HgCl_2$ is also examined in the case of (I). At the acid concn., $FeCl_3$ or $CuCl_2$ is as efficient as CuCl. $CoCl_2$ in the blue complex anionoid condition catalyses the reaction, whereas in the pink cationoid state it loses its catalytic influence. The results support the mechanism previously suggested (A., 1942, II, 52, 254). A. T. P.

Decomposition of diazotised 1 : 6-dinitro-2-naphthylamine by precipitated copper in organic solvents. H. H. Hodgson and H. S. Turner (*J.C.S.*, 1944, 10—11).—1 : 6 : 2-$(NO_2)_2C_{10}H_5{\cdot}N_2HSO_4$ is added to pptd. Cu in a solvent at 15° (cf. Cu_2O method; A., 1943, II, 158); if MeOH is used, no CH_2O is formed and a yield of 58% of 1 : 6-$C_{10}H_6(NO_2)_2$ results. Yields are recorded using other solvents, *e.g.*, EtOH (57·5), Pr$^\beta$OH (54·5), Bu^{a}OH (36·5), COMeEt (44·5), and $Cl{\cdot}[CH_2]_2{\cdot}OH$ (36%) (cf. *loc. cit.*). 2 : 1-$NO_2{\cdot}C_{10}H_6{\cdot}NH_2$

is deaminated similarly to 2-$C_{10}H_7\cdot NO_2$ in MeOH (35) or EtOH (33·5%). A. T. P.

Colour and constitution. VIII. Coupling of the four *m*-halogenophenols and the chromoisomerism of the 3-halogeno-4-benzeneazophenols, explained on resonance theory. H. H. Hodgson (*J. Soc. Dyers and Col.*, 1944, **60**, 43—45; cf. A., 1943, II, 361).—The unique mono-coupling of *m*-$C_6H_4F\cdot OH$ in position 4, and the mono- and di-coupling of the other three *m*-$C_6H_4Hal\cdot OH$ in the 4- and 2 : 4-positions, are discussed from the viewpoint of H bonding and theory of resonance. The consequent chromoisomerism which arises both in the 3-halogeno-4-benzeneazophenols and in 3 : 2-$NO_2\cdot C_{10}H_6\cdot NH_2$ is explained. A. T. P.

***p*-Diphenylyl iodoacetate.** L. C. Hensley and S. E. Hazlet (*J. Amer. Chem. Soc.*, 1943, **65**, 2256).—$CH_2Br\cdot CO_2\cdot C_6H_4Ph$-*p* or $CH_2Cl\cdot CO_2\cdot C_6H_4Ph$-*p* with KI in $COMe_2$ at room temp. and then the b.p. give 77·8 and 18·3%, respectively, of p-*diphenylyl iodoacetate*, m.p. 113·5—114·3°. R. S. C.

Reduction products of *o*-nitrophenyl esters of arylsulphonic acids. L. C. Raiford and J. R. Shelton (*J. Amer. Chem. Soc.*, 1943, **65**, 2048—2051).—*o*-$NO_2\cdot C_6H_4\cdot O\cdot SO_2Ar$ (*A*) and its derivatives are reduced by $SnCl_2$–EtOH–conc. HCl to NH_2-esters without migration of acyl; mixed aliphatic acyl arylsulphonyl derivatives of *o*-$NH_2\cdot C_6H_4\cdot OH$ and its substitution products are stable. Latimer's theory (A., 1930, 9) does not account for this difference between arylsulphonyl and purely aliphatic derivatives. (*A*) are prepared from *o*-$NO_2\cdot C_6H_4\cdot OH$ etc. and $ArSO_2Cl$ in C_5H_5N. The following are described. *o*-$NO_2\cdot C_6H_4$ benzene-, m.p. 64° (lit. 75°), *p*-toluene-, m.p. 81°, p-*bromo*-, m.p. 98·5°, and m-*nitro-benzene-sulphonate*, m.p. 88°; 4 : 6-*dibromo*-2-*nitrophenyl benzenesulphonate*, m.p. 131·5°, p-*toluenesulphonate*, m.p. 141°, p-*bromo*-, m.p. 131°, and m-*nitro-benzenesulphonate*, m.p. 113°; 3-*bromo*-5-*nitro*-p-*tolyl benzenesulphonate*, m.p. 155°, p-*toluenesulphonate*, m.p. 127°, p-*bromo*-, m.p. 151°, and m-*nitro-benzenesulphonate*, m.p. 98°; 4-*bromo*-2-*nitrophenyl*, m.p. 88—89°, 4-*nitro*-m-*tolyl*, m.p. 83—84°, 6-*bromo*-4-*nitro*-m-*tolyl*, m.p. 119—120°, and 2 : 6-*dibromo*-4-*nitro*-m-*tolyl benzenesulphonate*, m.p. 124—126°; 4-*bromo*-2-*nitrophenyl*, m.p. 101°, 6-*bromo*-4-*nitro*-m-*tolyl*, m.p. 86—87°, and 4-*nitro*-m-*tolyl* p-*bromobenzenesulphonate*, m.p. 91—92°; o-*aminophenyl benzenesulphonate*, m.p. 86°, *p*-toluenesulphonate, m.p. 98·5° (lit. 102°), p-*bromo*-, m.p. 111—112°, and m-*amino-benzenesulphonate*, m.p. 125—126°; 6-*bromo*-4-*amino*-m-*tolyl*, m.p. 100°, and 3-*bromo*-5-*amino*-p-*tolyl benzenesulphonate*, m.p. 95°; 4 : 6-*dibromo*-2-*aminophenyl* p-*toluene*-, m.p. 129—130°, and p-*bromobenzene-sulphonate*, m.p. 128°; 3-*bromo*-5-*amino*-p-*tolyl* p-*toluene*-, m.p. 88°, and p-*bromobenzene-sulphonate*, m.p. 112—113°. R. S. C.

Synthesis and properties of aryl vinyl ethers. M. F. Schostakovski and M. S. Burmistrova (*J. Appl. Chem. Russ.*, 1942, **15**, 260—266).—PhOH containing 10—15% of H_2O, C_6H_6 at 10—18 atm., and NaOH afford at 180° OPh·CH:CH_2, b.p. 155—156° (only slightly hydrolysed by 2% H_2SO_4); if PhOH is dry, a polymer is formed. Similarly are prepared o-*tolyl*, b.p. 167—168·5°, m-*tolyl*, b.p. 173—174·5°, p-*tolyl*, b.p. 175·5°, *α-naphthyl*, b.p. 257—258·5°, and *benzyl* (I), b.p. 183—184°, *vinyl ether*. The mol. refraction of the ethers, except (I), is by 0·8—1 > expected, and all the ethers, except (I), polymerise on heating. J. J. B.

Preparation of 6-nitro-1-naphthol, improved methods for the decomposition of diazo-naphthols, and new reactions of nitro-naphthols. H. H. Hodgson and H. S. Turner (*J.C.S.*, 1944, 8—10).—6-Nitro-2-diazo-1-naphthol (I) [from 1 : 6 : 2-$(NO_2)_2C_{10}H_5\cdot NH_2$], explodes at 150—151° (lit. 142—145°, 151—157°), is converted by Cu_2O–EtOH in AcOH–H_2SO_4 at 55—80° into 6 : 1-$NO_2\cdot C_{10}H_6\cdot OH$ (II), new m.p. 181—182° (*acetate*, m.p. 121°; *benzoate*, m.p. 147·5—148°). (I) and aq. HCl–CuCl at 100° (bath) give 2-*chloro*-6-*nitro*-1-*naphthol*, m.p. 179—180°, converted by Br–AcOH at 60—90° into its 4-*Br*-derivative, m.p. 199°. 2-*Bromo*-6-*nitro*-1-*naphthol*, m.p. 164·5—165·6°, is similarly obtained from (I). (II) and Br–AcOH at room temp. give the 4-*Br*-derivative, m.p. 238°, and at 100° (bath) afford 2 : 4-*dibromo*-6-*nitro*-1-*naphthol*, m.p. 210° [also obtained from (I) and Br–AcOH at 110° without evolution of HBr]. (I) in AcOH–H_2SO_4 and saturated aq. KI (+ Cu powder) at 95° yield 2-*iodo*-6-*nitro*-1-*naphthol*, m.p. 214—215° (decomp.) (discolours >200°). (II) and $Hg(OAc)_2$–AcOH give 6-*nitro*-1-*naphthol*-4-*mercuriacetate*, m.p. >360° (shrinks at 300°), converted by I in 30% aq. KI at 90—100° into 4-*iodo*-6-*nitro*-1-*naphthol*, m.p. 214—216°. 4 : 5-*Dinitro*-1-*diazo*-2-*naphthol* (III) [from 2 : 4 : 5 : 1-$(NO_2)_3C_{10}H_4\cdot NH_2$], decomp. slowly if heated gradually, explodes at 160° on rapid heating, is converted by Al + a little Cu in boiling EtOH into 4 : 5 : 2-$(NO_2)_2C_{10}H_5\cdot OH$, m.p. 237—238° (lit. ~230°). 1-*Bromo*-4 : 5-*dinitro*-2-*naphthol*, m.p. 218—220°, is obtained from (III) and 30% HBr–CuBr at 100° (bath). *β*-$C_{10}H_7\cdot NH\cdot SO_2\cdot C_6H_4Me$-*p* with Br–AcOH at 90°, followed by hydrolysis (cold, conc. H_2SO_4) and diazotisation, affords 6-*bromo*-2-*diazo*-1-*naphthol*, m.p. 214° (decomp.) (darkens ~145°; shrinks ~160°), converted by Al–Cu–Devarda's alloy in boiling EtOH into 6 : 1-$C_{10}H_6Br\cdot OH$. 1 : 6 : 2-$(NO_2)_2C_{10}H_5\cdot NH\cdot SO_2\cdot C_6H_4Me$-*p* after hydrolysis, diazotisation, and immediate addition to *β*-$C_{10}H_7\cdot OH$ in aq. NaOH at <10° gives 1 : 6-*dinitro*-2-*naphthaleneazo*-*β*-*naphthol*, m.p. 310°. M.p. are corr. A. T. P.

Phenols of the heavy oil of coal tar. II. O. Kruber and A. Marx (*Ber.*, 1940, **73**, [*B*], 1175—1177).—Fractional extraction with 4—5% NaOH of a phenol mixture, b.p. 248—252°, leads to the isolation of 5-*hydroxyhydrindene* (I), b.p. 251°/760 mm., m.p. 54—55° [*phenylurethane*, m.p. 155°; *oxyacetic acid*, m.p. 157°; *benzoate* (II), m.p. 110°], and 3 : 4 : 5-*trimethylphenol* (III), b.p. 248°/758 mm., m.p. 106° (phenylurethane, m.p. 148°; *oxyacetic acid*, m.p. 149°). (III) forms mixed crystals with (I) which can be removed as (II). H. W.

ββ-**Di-*p*-hydroxyphenylpropane.**—See B., 1944, II, 65.

Alkylpyrocatechols.—See B., 1944, II, 65.

Invert soaps. IV. Quaternary salts of aminophenyl ethers. R. Kuhn and D. Jerchel (*Ber.*, 1940, **73**, [*B*], 1100—1105; cf. A., 1944, II, 95).—*o*-$NO_2\cdot C_6H_4\cdot OK$, *n*-$C_{12}H_{25}Cl$, and a little $ZnCl_2$ in EtOH at 180° give o-$NO_2\cdot C_6H_4$ (55—65%), b.p. 201—203°/3·5 mm., hydrogenated (PtO_2; EtOH) to o-$NH_2\cdot C_6H_4$ n-$C_{12}H_{25}$ *ether*, m.p. 39°, b.p. 188—189°/3 mm. (*hydrochloride*), which with Me_2SO_4 at ~150° gives *o*-$NMe_2\cdot C_6H_4$ *n*-$C_{12}H_{25}$ *ether* (80%), b.p. 220°/3 mm. [*methylmethosulphate* (I), m.p. 102—104°]. *p*-$NO_2\cdot C_6H_4\cdot OK$ gives similarly p-$NO_2\cdot C_6H_4$, m.p. 55°, and thence *p*-$NH_2\cdot C_6H_4$ (*hydrochloride*, m.p. 103—106°), and (by Me_2SO_4) *p*-$NMe_2\cdot C_6H_4$ *n*-$C_{12}H_{25}$ ether [*methylmethosulphate* (II), m.p. 118—120°]. *m*-$NMe_2\cdot C_6H_4\cdot OK$ gives m-$NMe_2\cdot C_6H_4$ n-$C_{12}H_{25}$ *ether*, m.p. 28—29° [*methylmethosulphate* (III), m.p. 82—83°]. The bactericidal and bacteriostatic activity of (I)—(III) are quantitatively similar to those of *n*-$C_{12}H_{25}\cdot NMe_2Br\cdot CH_2Ph$. R. S. C.

Derivatives of 4 : 4′-diaminodiphenyl sulphone.—See B., 1944, III, 33.

Role of neighbouring groups in replacement reactions. VII. Methoxyl group.—See A., 1944, II, 90.

Action of anisole with *αaa*-trichloro-*β*-methyl-Δ^{β}-propene.—See A., 1944, II, 89.

Behaviour of hydrogenated anisoles towards lithium phenyl.—See A., 1944, II, 114.

Synthesis of 1 : 4-epoxy*cyclo*hexane. R. C. Olberg, H. Pines, and V. N. Ipatiev (*J. Amer. Chem. Soc.*, 1943, **65**, 2260).—Passing *cis*- or *trans-cyclo*hexane-1 : 4-diol over activated Al_2O_3 at 275° gives 28 or 73%, respectively, of 1 : 4-*epoxy*cyclo*hexane*, b.p. 120·1°/760 mm., converted by 48% HBr into *trans*-1 : 4-dibromo*cyclo*hexane. R. S. C.

Restricted rotation in arylolefines. VII. New synthesis of hindered *β*-substituted *β*-arylacrylic acids. R. Adams and C. W. Theobald (*J. Amer. Chem. Soc.*, 1943, **65**, 2208—2211; cf. A., 1943, II, 10).—Di-*o*-substitution only slightly reduces the ease with which $CPh_2{:}C\cdot CO_2H$ undergoes addition reactions. 2 : 4 : 6 : 1-$C_6H_2Me_3\cdot COMe$ and PCl_5 at 60° (3 hr.) and then 100° (45 min.) give 2 : 4 : 6 : 1-$C_6H_2Me_3\cdot CCl{:}CH_2$ (50%), b.p. 122—124°/25 mm., -$C_6H_2Me_3\cdot CO\cdot CH_2Cl$ (19%), m.p. 62—63°, and some *α-mesitylvinyl* H_2 *phosphate*, m.p. 229—232°. 2 : 4 : 6 : 1-$C_6H_2Me_3\cdot C{:}CH$ with MgEtBr–Et_2O and then CO_2 at <0°/2·5—3 atm. gives *mesitylpropiolic acid* (I) (43%), m.p. 165—167° (decomp.), which with gaseous HCl in AcOH at 80—90° gives *β-chloro-β-mesitylacrylic acid* (67%), m.p. 145—146°, obtained also (71%) from 2 : 4 : 6 : 1-$C_6H_2Me_3\cdot CO\cdot CH_2\cdot CO_2H$ by $POCl_3$–PCl_5 at 0°. With HBr–AcOH (79% yield) or, less well, aq. HBr at room temp. (I) gives *β-bromo-β-mesitylacrylic acid*, m.p. 135—135·5°. 2 : 3 : 4 : 6 : 1-$C_6HMe_4\cdot COMe$ (II) and PCl–PCl_3–$POCl_3$ at, successively, 0°, room temp., 55°, and 65—70° give *α*-iso*durylvinyl chloride* (III), b.p. 225°/745 mm., with *ω-chloroacetoisodurene*, m.p. 88—88·5°, b.p. 144°/6 mm., and ? *α*-iso*durylvinyl* H_2 phosphate, m.p. 184—184·5°. NaOEt converts (III) in boiling EtOH into iso*durylacetylene* (~65%), b.p. 86°/1 mm., which affords, as above, iso*durylpropiolic* (67%), m.p. 164—164·5° (decomp.), and thence *β-chloro-* (90%), m.p. 185°, and (by aq. HI at room temp.) *β-iodo-β-*iso*durylacrylic acid* (90%), m.p. 183—184°. MgEtBr–Et_2O and then CO_2 converts (II) into *β-keto-β-*iso*durylpropionic acid* (71%), m.p. 113—114° (decomp.). M.p. are corr.

Synthesis of amino-acids from substituted cyanoacetic esters.—See A., 1944, II, 91.

Condensation of aldehydes with malonic acid. XV. Condensation of 5-bromo- and 3 : 5-dibromo-salicylaldehyde; influence of dissimilar groups. K. C. Pandya and (Miss) R. B. K. Pandya (*Proc. Indian Acad. Sci.*, 1943, **18**, **A**, 164—170; cf. A., 1941, II, 170).—Condensation of *o*-OH·C_6H_4·CHO with $CH_2(CO_2H)_2$ is facilitated by the presence of Br or Cl in the aromatic nucleus. By reason of the ready sublimation of 2 : 5 : 1-OH·C_6H_3Br·CHO condensation with $CH_2(CO_2H)_2$ in presence of a little C_5H_5N at 100° proceeds somewhat slowly, giving 5-*bromo*-2-*hydroxycinnamic acid* (I), m.p. 150—152° (yield 50—55%) (no colour with $FeCl_3$; decolorises Baeyer's reagent), and 5-*bromosalicylidenemalonic acid*, m.p. 175° (decomp.) (yield 24%), which passes at 180° into (I). At 100—105° in absence of a

condensing agent the reactants afford 6-*bromocoumarin*-3-*carboxylic acid*, m.p. 200° (yield 92·5%), with small amounts of a compound, m.p. 241° (decomp.). 2 : 3 : 5 : 1-OH·$C_6H_2Br_2$·CHO (**II**), fused NaOAc, and Ac_2O at 170—180° afford 6 : 8-dibromocoumarin, m.p. 176°, in ~33% yield. (**II**), $CH_2(CO_2H)_2$, and a little C_5H_5N at 110° give a substance, m.p. 323—327°, darkens at 210°, which contains Br but not OH, CHO, or CO_2H, 3 : 5-*dibromo*-2-*hydroxycinnamic acid*, m.p. 185—187° (yield 31%), and 3 : 5-*dibromosalicylidenemalonic acid*, m.p. 157—159° (yield 22%). In absence of a condensing agent the reactants afford 6 : 8-*dibromocoumarin*-3-*carboxylic acid*, apparently dimorphous, m.p. 224—226°. H. W.

Reaction of sodium triphenylmethyl with esters of $\alpha\beta$-unsaturated acids. W. D. McPhee and E. G. Lindstrom (*J. Amer. Chem. Soc.*, 1943, **65**, 2177—2180).—CPh_3Na does not cause enolisation of CHMe:CH·CO_2Et in Et_2O, but by 1 : 4-addition gives [CPh_3·CHMe·CH·CO_2Et]Na (**I**), whence H_2O and then boiling 10% KOH–EtOH gives *β-triphenylmethyl*-n-*butyric acid* (**II**), m.p. 213·5—215·5° (214—216°) after sintering (p-*bromophenacyl* ester, m.p. 174—176° after sintering) (cf. Michael *et al.*, A., 1943, II, 192). Adding BzCl to (**I**) *in situ* gives a glass, whence distillation gives $CHPh_3$ and impure CPh_3·CHMe·CHBz·CO_2Et (**III**), hydrolysed by KOH in boiling 75% EtOH to (**II**) and BzOH; hydrolysis of (**III**) to a ketone was impracticable. ~2 mols. of CH_2:CH·CO_2Me are required to discharge the colour of 1 mol. of CPh_3Na; hydrolysis of the product affords, with difficulty, *γγγ-triphenyl*-n-*butyric* (**IV**) (16%), m.p. 153—156° (p-*bromophenacyl* ester, m.p. 193·5—194·5°), and *α-β'β'β'-triphenylethylglutaric acid* (18%), m.p. 205—206° (*bis*-S-*benzylthiuronium* salt, m.p. 144—144·5°). CPh_3Na and $(CH_2)_2O$ in Et_2O give *γγγ-triphenyl*-n-*propyl alcohol* (96%), m.p. 107—108°, b.p. 208—212°/3 mm., converted by red P–I at 165° into the iodide, m.p. 173·5—174·5° (cf. Wooster *et al.*, A., 1934, 1095), the Grignard reagent of which with gaseous CO_2 gives 19% of (**IV**), sinters 148°, m.p. 154—156° (*p*-bromophenacyl ester, sinters 192°, m.p. 194—195·5°). R. S. C.

Reformatsky reaction with benzylideneaniline. H. Gilman and M. Speeter (*J. Amer. Chem. Soc.*, 1943, **65**, 2255—2256).—CHPh:NPh, $CH_2Br·CO_2Et$ (gives 54% yield) or $CH_2Br·CO_2·CH_2Ph$ (gives 40% yield), and Zn in boiling PhMe give, after or without hydrolysis, β-anilino-β-phenylpropiolactam, m.p. 154°. Use of CHMeBr·CO_2Et gives 85% of β-anilino-β-phenyl*iso*butyrolactam, m.p. 109—110°. R. S. C.

Anhydrides of peptides and dehydrogenated peptides. J. E. Tietzman, D. G. Doherty, and M. Bergmann (*J. Biol. Chem.*, 1943, **151**, 387—394).—Acetyldehydrophenylalanyldehydrophenylalanine (**I**) and C_5H_5N–H_2O (1 : 1) at 100° (bath), followed by 2*N*-HCl at 0°, afford *anhydroacetyldehydrophenylalanyldehydrophenylalanine* (**II**), m.p. 210—212° (decomp.), also obtained similarly, but more slowly, at 37·5° (20 days), or from the azlactone of (**I**) at 100° (bath). Hydrogenation ($2\ H_2$; Pd-black in EtOH at 20—25° for 150 hr.) of (**II**) yields *anhydroacetylphenylalanylphenylalanine*, m.p. 203—204° (decomp.) (*Me* ester, m.p. 135—137°) (decomposed by boiling HCl to phenylalanine), and an *acetylphenylalanylphenylalanine* (**III**), m.p. 246—248° (decomp.). The azlactone of the Bz analogue of (**I**) and C_5H_5N–H_2O (1 : 2) at 100° (bath) give *anhydrobenzoyldehydrophenylalanyldehydrophenylalanine*, m.p. 258—259° (decomp.). The crude azlactone from glycine, PhCHO, and Ac_2O–NaOAc with boiling H_2O (2 hr.) (cf. Dakin, A., 1929, 811) gives a *product*, $C_{20}H_{16}O_3N_2$, m.p. 254—255° (decomp.) (structure suggested); it forms Na, NH_4, and C_5H_5N salts. The azlactone of acetylbis(dehydrophenylalanyl)-dehydrophenylalanine and $COMe_2$ in N-NaOH at room temp. yield *anhydrobis*(*dehydrophenylalanyl*)*dehydrophenylalanine azlactone*, m.p. 288—289° (decomp.). Hydrogenation ($2\ H_2$; Pd in aq. $NaHCO_3$) of (**I**) or acetyldehydrophenylalanyl-*dl*-phenylalanine affords (**III**) and an *isomeride*, m.p. 183—185°. Acetyldehydrophenylalanylglycine at 180° in vac. gives only a tar, and neither it nor its Bz analogue could be transformed by C_5H_5N–H_2O into anhydropeptides. A. T. P.

Cyclic fatty acids. *cyclo*Hexylgeranylacetic acid. L. Leder-Pakendorf (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **31**, 757—760).—Adding Et *cyclo*hexylmalonate and then geranyl chloride to Na powder in xylene–PhMe gives *Et* cyclo*hexylgeranylmalonate* [*Et α-carbethoxy-α*-cyclo*hexyl-δθ-dimethyl-*$\Delta^{\gamma\eta}$-n-*decadienoate*], b.p. 201—203·5°/5 mm., the derived (50% KOH) oily acid from which at 40—150° gives α-cyclo*hexyl-δθ-dimethyl-*$\Delta^{\gamma\eta}$-*decadienoic acid* (**I**), b.p. 213—214°/7 (? 17) mm. (*Et* ester, b.p. 215—218°/25 mm.), reduced by H_2–Pd–Pt–C in EtOH to α-cyclo*hexyl-δθ-dimethyl*-n-*decoic acid* (**II**), b.p. 218—219°/14 mm. (**I**) and (**II**) are only feebly toxic, but are effective against *Lupus vulgaris*, *Lepra*, and [(**I**) much more effective than (**II**)] tubercle bacilli. R. S. C.

Chemotherapeutic study of *p*-nitrobenzoyl and related compounds. C. Siebenmann and R. J. Schnitzer (*J. Amer. Chem. Soc.*, 1943, **65**, 2126—2128).—*cyclo*Hexanol (2 mols.) and *p*-$NO_2·C_6H_4$·COCl (**I**) (1 mol.) in C_5H_5N at <20° and then at the b.p. give cyclo*hexyl* p-*nitrobenzoate* (**II**), m.p. 51·5—52·5°. Resorcinol (2 mols.) and (**I**) (1 mol.) in C_5H_5N at 100° give *resorcinol mono-*, m.p. 175—177°, and some *di*-p-*nitrobenzoate*, m.p. 185—186° [best obtained by use of an excess of (**I**)]. The following are similarly prepared. *Pyrocatechol mono-*, m.p. 151—152°, and *di-*, m.p. 162—165°, quinol mono-, m.p. 190—194°, and di-, m.p. 252—257°, *pyrogallol mono-*, m.p. 193—197°, and *tri-*, m.p. 229—231°, 4-hexylresorcinol mixed (**III**) (m.p. 60—72°) mono- and di-, *inositol hexa-* (prep. without a solvent at 180—200°), m.p. 310—315°, -p-*nitrobenzoate*; cyclo*hexyl* 3 : 5-*dinitrobenzoate*, m.p. 109—111°; p-*nitrobenz-morpholide*, m.p. 101—106°, -*piperidide*, m.p. 115—118°, and -cyclo*hexylamide*, m.p. 203—204°; 3 : 5-*dinitrobenz-morpholide*, m.p. 184—187°, and -*piperidide*, m.p. 143—144·5°; 1 : 4-*di*-p-*nitrobenzoylpiperazine*, m.p. 318°. *p*-$NH_2·C_6H_4·SO_2·NH_2$ (**IV**) (0·1 l) and (**I**) (0·23 mol.) in C_5H_5N at <30° and then 100° give N^1N^4-*di*-, m.p. 268° (decomp.), hydrolysed by boiling 30% NaOH to N^1-*p*-nitrobenzoylsulphanilamide (**V**), m.p. 218—219° (lit. 235—240°). 1 mol. each of (**I**) and (**IV**) in C_5H_5N give N^4-p-*nitrobenzoylsulphanilamide*, m.p. 260°. N^1-Benzoyl- (**VI**), m.p. 178—180° (lit. 181·2—182·3°), and N^1N^4-dibenzoyl-sulphanilamide, m.p. 252° (decomp.) (lit. 268—270°), are also prepared. Most of these compounds have little or no anticoccal activity. (**II**) is slightly active against strepto- but not against pneumo-cocci. (**III**) is effective against pneumococci. (**V**) is extremely effective against meningococci in mice, and (**VI**) is sp. against pneumococci. The N^1N^4-derivatives of (**IV**) are quite inactive, as are the 3 : 5-dinitrobenzoyl derivatives. R. S. C.

Isomorphism of organic compounds. VI. H. Lettré [with H. Barnbeck, P. Lehmann, and M. Stier] (*Ber.*, 1940, **73**, [*B*], 1150—1152).—*p*-OMe·$C_6H_4·CO_2H$ (**I**) gives eutectics with BzOH and *p*-$C_6H_4R·CO_2H$ (R = OH, Me, Cl, Br, and I). OMe therefore resembles OH in inability of isomorphous replacement by other substituents. (**I**) forms additive compounds (1 : 1) with *o-*, *m-*, and *p*-$NO_2·C_6H_4·CO_2H$. *r*-OH·CHPh·CO_2H (**II**) gives only a eutectic with *r-p*-OMe·C_6H_4·CH(OH)·CO_2H (**III**). Similar observations are made with (+)-*p*-OMe·C_6H_4·CH(OH)·CO_2H and (+)- and (−)-OH·CHPh·CO_2H. (**II**) and (**III**) form a system of two true racemates in which the racemic forms are not isomorphous. The sterically similar forms do not give mixed crystals and a partial racemate does not arise from the sterically opposite modifications. H. W.

Rearrangement of benzyl ethers of salicylic acids. D. S. Tarbell and V. P. Wystrach (*J. Amer. Chem. Soc.*, 1943, **65**, 2146—2149).—2 : 3 : 5 : 1-OH·$C_6H_2Cl_2·CO_2$H (**I**), CH_2PhCl, K_2CO_3, and NaI in boiling COMeEt–H_2O give *Me* 3 : 5-*dichloro*-2-*benzyloxybenzoate*, m.p. 42·5—43·5°, hydrolysed by KOH–H_2O–MeOH to the *acid* (**II**), m.p. 148—148·5°. At 153° (**II**) gives *CH_2Ph* 3 : 5-*dichlorosalicylate* (**III**) (65—72%), m.p. 109·5—110·5° [also obtained from (**I**) (as Na salt) by $CH_2Ph·OH$ and a little NEt_3 at 135°], (**I**) (20%), and 8—10% of CO_2, but no other decarboxylation product. In $NPhMe_2$ at 155° (**II**) gives 51% of (**III**) and 25% of (**I**); (**III**) is also obtained slowly in boiling AcOH, but (**II**) is unchanged in PhMe–xylene at 116—117°. *o*-$CH_2Ph·O·C_6H_4·CO_2$H at 185—190° gives *o*-OH·$C_6H_4·CO_2·CH_2Ph$ (35%), *o*-OH·$C_6H_4·CO_2$H (17—~35%), and 5 : 2 : 1-$CH_2Ph·C_6H_3(OH)·CO_2·CH_2Ph$ (a little; identified by hydrolysis). 5 : 2 : 1-$NO_2·C_6H_3(OH)·CO_2$Et, m.p. 97—97·5° (lit. 93°), gives, as above, *Et* 5-*nitro*-2-*benzyloxybenzoate*, m.p. 75—75·5°, which with KOH–H_2O–MeOH at the b.p. gives 5 : 2 : 1-$NO_2·C_6H_3(OMe)·CO_2$H, m.p. 159·5—160·5° (lit. 161°), but at room temp. gives 5-*nitro*-2-*benzyloxybenzoic acid*, m.p. 166—166·5°. At 175° this gives *CH_2Ph* 5-*nitrosalicylate* (63%), m.p. 83·5—85·5° [also prepared from 5 : 2 : 1-$NO_2·C_6H_3(OH)·CO_2$Na and CH_2PhCl], and 5 : 2 : 1-$NO_2·C_6H_3(OH)·CO_2$H (28%). The reaction mechanism is discussed. M.p. are corr. R. S. C.

Effect of heat on the β-naphthylmethyl and 9-phenanthrylmethyl ether of 3 : 5-dichlorosalicylic acid. D. S. Tarbell and V. P. Wystrach (*J. Amer. Chem. Soc.*, 1943, **65**, 2149—2153).—The 9 : 10-ethylenic linking of phenanthrene is sufficiently "aliphatic" to cause rearrangement of 9-phenanthrylmethyl ethers to resemble that of allyl (A., 1942, II, 258) rather than that of CH_2Ph ethers (cf. preceding abstract). This is not so for the 1 : 2-linking of $C_{10}H_8$, since β-$C_{10}H_7·CH_3$ resemble CH_2Ph ethers. β-$C_{10}H_7·CH_2Cl$ with 2 : 3 : 5 : 1-OH·$C_6H_2Cl_2·CO_2$Me (**I**) and NaOH in aq. COMeEt and then KOH–MeOH–EtOH gives 3 : 5-*dichloro*-2-*β-naphthylmethoxybenzoic acid* (**II**) (50%), m.p. 142—142·5° (decomp.), which at 147—148° gives *β-naphthylmethyl* 3 : 5-*dichlorosalicylate* (**III**) (67%), m.p. 138·5—139° [identified by hydrolysis to 2 : 3 : 5 : 1-OH·$C_6H_2Cl_2·CO_2$H (**IV**) and β-$C_{10}H_7·CH_2$·OH], CO_2 (9·5%), and (**IV**) (~10%). (**III**) is also obtained when (**II**) is crystallised from AcOH. HCl passed into phenanthrene, conc. HCl, and 40% CH_2O at 94° gives 9-chloromethylphenanthrene (**V**) (21%), m.p. 101·5—102° [picrate, m.p. 101·5—102° (lit. 99·5—100·5°)], which with (**I**), NaI, and K_2CO_3 in aq. COMeEt gives *Me* 3 : 5-*dichloro*-2-9'-*phenanthrylmethoxybenzoate* (56%), m.p. 162·5—163·5°. Hydrolysis with alkali then yields the derived *acid* (**VI**), m.p. 174·5—175°, which at 229° gives CO_2 (75%), (**IV**) (29·8%), and 9-3' : 5'-*dichloro*-2'-*hydroxyphenyl*-10-*methyl*-[? 9-3' : 5'-*dichloro*-2'-*hydroxybenzyl*-]*phenanthrene* (41%), m.p. 136·5—137·5° (*acetate*, m.p. 208—208·5°). (**VI**) is unchanged in boiling AcOH. 9-Phenanthroyl chloride, 2 : 4 : 1-$C_6H_3Cl_2$·OH (**VII**), and $AlCl_3$ in CS_2 give 2 : 4 : 1-*$C_6H_3Cl_2$* 9-*phenanthroate* (14%), m.p. 183—184°, which with EtOH gives some of the *Et* ester, m.p. 114·5—115°. (**V**), (**VII**), NaI, and K_2CO_3 in aq. COMeEt give 9-2' : 4'-*dichlorophenoxymethylphenanthrene* (60%), m.p. 125—125·5°, which at 279—280° (not 240°) yields (**VII**) as sole product isolated. Mg,

(V), and a trace of MeI in boiling Et_2O–C_6H_6 give, after treatment with aq. NH_4Cl, *αβ-di-9-phenanthrylethane* (59%), m.p. 252·5—254·5°, and a little (?) 9-methylphenanthrene. Zn–HCl–EtOH is without effect on (V). M.p. are corr. R. S. C.

Synthesis of phenolic acid esters. I. Depsides. C. J. Cavallito and J. S. Buck (*J. Amer. Chem. Soc.*, 1943, **65**, 2140—2142).—$OH{\cdot}C_6H_4{\cdot}CO_2Na$ and CH_2PhCl (1·1 mol.) in boiling aq. EtOH give up to 40% of CH_2Ph *p-*, m.p. 111°, *o-*, b.p. 158°/3 mm., and *m-hydroxybenzoate*, m.p. 70°. 2 : 4 : 1-$(OH)_2C_6H_3{\cdot}CO_2H$ and CH_2PhCl (1·05 mol.) in boiling KOH–EtOH–H_2O give *CH_2Ph* 2 : 4-*dihydroxybenzoate*, m.p. 60°, b.p. 215°/2 mm. Similar use of an excess of CH_2PhCl gives *CH_2Ph* p-*benzyloxybenzoate*, m.p. 115°, hydrolysed by alkali to *p*-$CH_2Ph{\cdot}O{\cdot}C_6H_4{\cdot}CO_2H$, m.p. 188°. Similarly are prepared *o*-benzyloxy-, m.p. 70°, 2 : 4-*di-*, m.p. 180°, and 3 : 4 : 5-tri-benzyloxybenzoic acid, m.p. 189°. The benzyloxy-acids with $SOCl_2$ give the acid chlorides, which with CH_2Ph esters of OH-acids give $CH_2Ph{\cdot}O{\cdot}C_6H_4{\cdot}CO_2{\cdot}C_6H_4{\cdot}CO_2{\cdot}CH_2Ph$ etc., whence H_2–spongy Pd in dioxan at 50°/40 lb. gives the free depsides. Thus are obtained: *p*-benzyloxy-, m.p. 110°, and 3 : 4 : 5-*tribenzyloxy-benzoyl chloride*, m.p. 115°; *CH_2Ph* p-, m.p. 166°, m-, m.p. 107°, and o-p′-*benzyloxybenzoyloxybenzoate*, m.p. 73°; *CH_2Ph* p-o′-*benzyloxybenzoyloxy-*, m.p. 71°, 2 : 4-*di*-p-*benzyloxybenzoyloxy-*, m.p. 111°, and p-3′ : 4′ : 5′-*tribenzyloxybenzoyloxy-benzoate*, m.p. 107°; *p-*, m.p. ~270°, *m-* m.p. 247°, and o-p′-*hydroxybenzoyloxybenzoic acid*, m.p. 180°; p-o′-*hydroxy-*, m.p. 210°, p-3′ : 4′ : 5′-*trihydroxy-*, m.p. 255—260°, and 2 : 4-*di*-p-*hydroxy-benzoyloxybenzoic acid*, m.p. ~210°. R. S. C.

Action of sodium on ethyl β-methylbutane-αβδ-tricarboxylate. III. Synthesis of *cis-allo*santenic acid. IV. R. N. Chakravarti (*J. Indian Chem. Soc.*, 1943, **20**, 243—246; 247—249; cf. A., 1943, II, 371).—III. $CO_2Et{\cdot}CH_2{\cdot}CMe(CN){\cdot}CH(CN){\cdot}CO_2Et$ and EtOH–NaOEt–MeI at room temp., then boiling, give *Et_2* *γδ-dicyano-γ-methylpentane-αδ-dicarboxylate*, b.p. 185°/5 mm., converted by boiling conc. HCl, followed by EtOH–H_2SO_4 at 110°, into *Et_3* *γ-methylpentane-αγδ-tricarboxylate* (I), b.p. 154°/5 mm. [free acid, m.p. 178° (cf. Sen-Gupta, A., 1933, 1049)]. (I) and Na in boiling C_6H_6 give *Et_2* 2 : 3-*dimethyl*cyclo*pentanone*-3 : 5-*dicarboxylate*, b.p. 135°/4 mm., which with boiling 6% HCl affords 2 : 3-dimethyl*cyclo*pentanone-3-carboxylic acid, a liquid (*semicarbazone*, decomp. 204°); its *Et* ester (HCl–EtOH), b.p. 99°/4 mm. and anhyd. HCN (+ a little KCN) at 9° yield a cyanohydrin, dehydrated by $POCl_3$–C_5H_5N at 145—150° and then hydrolysed by boiling conc. HCl to a mixture, m.p. 140—145°, of santenenic and *iso*santenenic acid. The mixture is hydrogenated (PtO_2, AcOH, room temp., 1 atm.) to 2 : 3-dimethyl-*cyclo*pentane-1 : 3-dicarboxylic acid, converted by AcCl into *cis-allo*santenic anhydride (II), m.p. 92°, and some isomeric santenic acids. Hydrolysis of (II) with EtOH–KOH yields *cis-allo*santenic acid, m.p. 151—152° (cf. Enkvist, A., 1933, 822).

IV. $CO_2Et{\cdot}[CH_2]_2{\cdot}CMe(CO_2Et){\cdot}CH_2{\cdot}CO_2Et$ and Na–C_6H_6, followed by $CH_2Br{\cdot}CO_2Et$, give *Et_3* 4-*methyl*cyclo*pentanone*-2 : 4-*dicarboxylate*-2-*acetate*, b.p. 170°/5 mm., hydrolysed by boiling conc. HCl to 4-methyl*cyclo*pentanone-4-carboxylic-2-acetic acid (*Et_2* ester, b.p. 145°/6 mm.), reduced (Clemmensen) to 1-*methyl*cyclo-*pentane*-1-*carboxylic*-3-*acetic acid* (III), m.p. 124—125°. Et 3-methyl*cyclo*pentanone-3-carboxylate and $CH_2Br{\cdot}CO_2Et$–Zn afford esters, converted by $POCl_3$–C_5H_5N into unsaturated esters, b.p. 125°/4 mm., and thence by H_2–PtO_2–EtOH at room temp. and 1 atm., followed by boiling 10% aq. KOH–EtOH, into (III). (III) is probably identical with the acid, m.p. 126°, described by Banerjee (A., 1941, II, 16) as the 2-acetic acid. A. T. P.

Sulphonated esters, amides, and imides of *cis*-3 : 6-*endo*methylenehexahydrophthalic acid.—See B., 1944, II, 66.

Synthesis of condensed ring compounds. XI. A tricyclic compound [obtained] by the di-inene double addition reaction. W. Nudenberg and L. W. Butz (*J. Amer. Chem. Soc.*, 1943, **65**, 2059—2060; cf. A., 1943, II, 330).—δ-1-Hydroxy*cyclo*pentyl-β-methyl-Δ$^{\gamma}$-*n*-butinen-β-ol, b.p. 124°/5 mm., and KHSO$_4$ at 160—180° give δ-Δ^1-cyclo*pentenyl*-β-*methyl*-Δ$^{\alpha}$-*buten*-Δ$^{\gamma}$-*inene* (62%), b.p. 81°/13 mm., which with $(CH{\cdot}CO)_2O$–CO_2 at 110—120° and then 150—160° gives 8-*methyl*-7 : 12-cyclo*penta*[a]*naphthitadiene*-5 : 6 : 10 : 11-[1-*methyl*-5 : 6-*trimethylene*-2 : 3 : 4 : 6 : 7 : 8-*hexahydronaphthalene*-3 : 4 : 7 : 8-]*tetracarboxylic anhydride* (13%), m.p. 168—170° (vac.) [absorption max. at 2500 A. (ε 18,000) in EtOH]. δ-1-*Hydroxy*-2-*methyl*cyclo*pentyl*-β-*methyl*-Δ$^{\gamma}$-n-*butinen*-β-*ol* (prep. in 70% yield), b.p. 122—123°/1—2 mm., in boiling 15 : 37 (vol.) H_2SO_4–H_2O gives δ-2-methyl-Δ^1-*cyclo*pentenyl-β-methyl-Δ$^{\alpha}$-buten-Δ$^{\gamma}$-inene (38%), b.p. 85—95° (90°)/13—14 mm., which with Me_2 fumarate (3 mols.)–N_2 at 190—200 gives (?) *Me_4* 4 : 8-*dimethyl*-7 : 12-cyclo*penta*[a]-*naphthitadiene*-trans-trans-5 : 6 : 10 : 11- [1 : 6-*dimethyl*-5 : 6-*trimethylene*-2 : 3 : 4 : 6 : 7 : 8-*hexahydronaphthalene*-trans-trans-3 : 4 : 7 : 8]-*tetracarboxylate*, a glass, whence N_2H_4 yields no cryst. product. *Me_4* $\Delta^{8(14):9}$-chrysitadiene-*trans-trans*-6 : 7 : 11 : 12-tetracarboxylate and N_2H_4,H_2O in boiling MeOH give a *Me_2* ester *dihydrazide*, m.p. 161—168° (decomp.). M.p. are corr. R. S. C.

Preparation of *p*-aminobenzaldehyde, and the mechanism of the reactions of sodium polysulphides with *p*-nitrotoluene. H. G. Beard and H. H. Hodgson (*J.C.S.*, 1944, 4—5).—*p*-$C_6H_4Me{\cdot}NO_2$ and Na_2S_x in boiling aq. EtOH–NaOH (90 min.) give *p*-$NH_2{\cdot}C_6H_4{\cdot}CHO$ (I) in yields of 35—40 ($x = 1$), 45·3 ($x = 2$), 53·4 ($x = 3$), and 72—75% ($x = 4$); much by-product results when $x = 5$. In absence of an alcohol (EtOH is more efficient than MeOH or Pr$^{\alpha}$OH) or of free alkali the optimum yield of (I) falls to 31 or <10%, respectively. A mechanism of the reaction is postulated.

[With R. R. Davies.] (I) (52%) and its *o*-Cl-derivative (48%) are prepared by a modification of Geigy's process (G.P. 86,874), using the respective nitrotoluene and 17% aq. NaOH + S. A. T. P.

Reaction of *p*-bromophenacyl bromide with chloride ions. H. H. Pokras and H. I. Bernstein (*J. Amer. Chem. Soc.*, 1943, **65**, 2096—2097).—*p*-$C_6H_4Br{\cdot}CO{\cdot}CH_2Br$ (I) and NaCl or KCl (excess) in boiling 62% EtOH give p-*bromophenacyl chloride* (II), also obtained (m.p. 117—118°; 80%) from PhBr, $CH_2Cl{\cdot}COCl$, and $AlCl_3$. Use of 1 mol. of NaCl causes only partial conversion, but the reverse change could not be effected. Solubilities of (I) and (II) in 62% EtOH at 25° are 0·332±0·008 and 0·278±0·01 g. per 100 c.c., respectively. Mixtures of (I) and (II) melt at intermediate temp. (mixed m.p. diagram given). Formation of (II) may obscure identification of compounds contaminated with NaCl. R. S. C.

Fluorine derivatives of acetophenone and ethylbenzene. J. H. Simons and D. F. Herman (*J. Amer. Chem. Soc.*, 1943, **65**, 2064—2066).—Fluorination may be effected by active AgF ($AgF_{1\cdot6}$) in liquid HF or by F$_2$ in liquid HF. Gradual replacement of Cl in C_2PhCl_5 by F progressively increases the difficulty of further exchange; exchange starts at $C_{(\alpha)}$. $COPh{\cdot}CHBr_2$ and $AgF_{1\cdot6}$ in liquid HF at 75° (not other methods) give $COPh{\cdot}CHF_2$ (40%), b.p. 83—85°/29 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 221—223°), converted by warm 5% NaOH into $OH{\cdot}CHPh{\cdot}CO_2H$. COPhMe, F_2, and Ag_2O in HF at 0° give $COPh{\cdot}CHF_2$ (20·2%) with small amounts of CF_4 and BzF. $COPh{\cdot}CCl_3$ and $AgF_{1\cdot6}$ in HF at <0° give *ωω-dichloro-ω-fluoro-* (48·7%), b.p. 111—112°/24 mm., and *ω-chloro-ωω-difluoro-acetophenone* (8·5%), b.p. 84—85°/25 mm., both converted by warm 10% NaOH into BzOH but failing to give 2 : 4-dinitrophenylhydrazones; a little BzF is also formed; $COPh{\cdot}CF_3$ could not be obtained thus from $COPh{\cdot}CCl_3$ or the products. $COPh{\cdot}CCl_3$ and PCl_5 at 220° give C_2PhCl_5 (84%), b.p. 155—156°/15 mm., which with HF at 145°/>300 lb. gives *αβββ-tetrachloro-α-fluoroethylbenzene* (I) (51·1%), b.p. 246°/731 mm., 123—126°/14 mm., *βββ-trichloro-αα-difluoroethylbenzene* (II) (29·8%), b.p. 219°/731 mm., 100°/16 mm., and small amounts of BzF and (?) $CPhF_2{\cdot}CCl_2F$. With SbF_3–$SbCl_5$ at 170—180° (I) gives (II) (47·3%), *ββ-dichloro-ααβ-trifluoroethylbenzene* (III) (6·7%), b.p. 177—178°/731 mm., 94—95°/42 mm., and a little BzF. Repeated treatment of (II) with $AgF_{1\cdot6}$–HF at 180° gives 19·9% of *β-chloro-ααββ-tetrafluoro-* (IV), b.p. 152—153°/733 mm., 1·3% of *pentafluoro-ethylbenzene*, b.p. 128—129°/733 mm., and 16% (III), $SbCl_5$ and (III) in HF at 180°/>400 lb. give 15% of (IV) and a small amount of C_2PhF_5 (not obtained pure by this method). R. S. C.

Preparation and properties of mesityl-2 : 4 : 6-trimethylbenzylglyoxal [αγ-dimesitylpropane-αβ-dione]. R. P. Barnes and A. E. Brandon (*J. Amer. Chem. Soc.*, 1943, **65**, 2175—2177).—$CHR{:}CH{\cdot}COR$ (R = mesityl) and H_2O_2 in NaOH–H_2O–MeOH at 30° give *βγ-epoxy-αγ-dimesitylpropan-α-one*, geometrical *isomerides*, m.p. (I) 95° and (II) 110°; illumination of (I) in EtOH gives (II), but the reverse change could not be effected. In boiling NaOH–MeOH–H_2O, (II) gives *β-hydroxy-αγ-dimesityl-Δβ-propen-α-one* (III), m.p. 143°; (I) gives mainly the geometrical *isomeride* (IV), m.p. 128°, and a little (III). (III) and (IV) give red colours with $FeCl_3$–EtOH and are respectively ~70% and ~40% enolic (Kurt Meyer), but are not interconvertible. Br in MeOH converts (III) or (IV) into *γ-bromo-αγ-dimesitylpropane-αβ-dione* (V), yellow, m.p. 137—148°, converted by boiling conc. HCl–MeOH into the colourless enolic *form* (VI), m.p. 143°, and by KI and a little AcOH in $COMe_2$ into (III). (VI) gives a dark brownish-green colour with $FeCl_3$–EtOH and is ~5% enolic (Kurt Meyer). With boiling Ac_2O–KOAc, (V) or (VI) gives *γ-bromo-β-acetoxy-αγ-dimesityl-Δβ-propen-α-one*, m.p. 133—134°, whence boiling conc. HCl–MeOH yields (VI). R. S. C.

Preparation and properties of mesityl-*p*-methoxybenzylglyoxal. R. P. Barnes and H. Delaney (*J. Amer. Chem. Soc.*, 1943, **65**, 2155—2157).—2 : 4 : 6 : 1-$C_6H_2Me_3{\cdot}COMe$ and *p*-$OMe{\cdot}C_6H_4{\cdot}CHO$ in NaOH–H_2O–EtOH at room temp. give *mesityl* p-*methoxystyryl ketone*, m.p. 103—104°, which with H_2O_2 in NaOH–H_2O–EtOH at ~35° gives the *oxide*, an oil, converted by boiling NaOH–MeOH–H_2O in 10 min. into *β-hydroxy-γ-*p-*anisyl-α-mesityl-Δβ-propen-α-one*, m.p. 97—98°. This is 99% enolic (Kurt Meyer) in EtOH, with alkaline H_2O_2 gives *p*-anisic and mesitoic acids, and with Br–$CHCl_3$ gives *γ-bromo-γ-*p-*anisyl-α-mesitylpropane-αβ-dione*, an oil, converted by KOAc in boiling AcOH into *β-hydroxy-γ-acetoxy-γ-*p-*anisyl-α-mesityl-Δβ-propen-α-one* (I), m.p. 128—129°. (I) gives a red colour with $FeCl_3$, is 83% enolic, is unchanged by AcCl, but with boiling KOAc–Ac_2O gives *βγ-diacetoxy-γ-*p-*anisyl-α-mesityl-Δβ-propen-α-one* (II), m.p. 96°. Hydrolysis of (I) or (II) by conc. H_2SO_4 gives the white, cryst. enediol (III), which gives a bluish-green colour with $FeCl_3$, decolorises indophenol, and, when kept, is converted by autoxidation into an orange peroxide and then into deep yellow α-p-*anisyl-γ-mesityl-*

propane-αβγ-trione, m.p. 106°. (**III**) is thus much less stable than its *o*-anisyl analogue (A., 1943, II, 66). R. S. C.

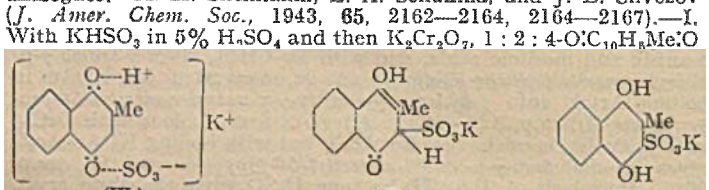
Polycyclic compounds. III. Benzonaphthone [*peri*naphthindenone] bromide, the primary product of interaction of bromine and benzonaphthone. A. M. Lukin (*Bul. Acad. Sci. U.R.S.S., Cl. Sci. chim.*, 1941, 565—572).—Contrary to Brass and Clar (A., 1940, II, 75) the primary interaction product of benzonaphthone and Br is the dibromide. The monobromide is an intermediate stage, as is the complex formed by the mono- and di-bromides. V. B.

Ionone. II. Optical resolution of *dl*-α-ionone. H. Sobotka, (Miss) E. Bloch, H. Cahnmann, (Misses) E. Feldbau, and E Rosen (*J. Amer. Chem. Soc.*, 1943, **65**, 2061—2062; cf. A., 1944, II, 78).—*dl*-α-Ionone and *l*-menthydrazide, $[\alpha]_D^{23}$ −76·7° in 95% EtOH, in boiling EtOH containing a little NaOAc and AcOH give the difficultly separable l-, m.p. 185°, $[\alpha]_D^{22}$ −320° in EtOH, and d-*α-ionone*-l-*menth-hydrazone*, m.p. 176°, $[\alpha]_D^{23}$ +230° in EtOH, whence distillation with *o*-$C_6H_4(CO)_2O$ in steam yields *l*-, $[\alpha]_D^{27}$ −406° (2 : 4-*dinitrophenylhydrazone*, m.p. 133°; *p*-chlorobenzoylhydrazone, m.p. 200—201°), and *d*-α-ionone, $[\alpha]_D^{23}$ +347° (2 : 4-*dinitrophenylhydrazone*, m.p. 129°; *p*-chlorobenzoylhydrazone, m.p. 196—198°), which differ in odour. β-Ionone-*l*-menth-hydrazone, m.p. 178°, [α] −35°, *dl*-α-ionone-2 : 4-dinitrophenylhydrazone, m.p. 143°, and -*p*-chlorobenzoylhydrazone, m.p. 214°, are also described. Use of the active compounds for investigating the α⟷β-ionone equilibration is discussed. R. S. C.

Volatile vegetable substances. XXVI. Ionones. Y. R. Naves and P. Bachmann (*Helv. Chim. Acta*, 1943, **26**, 2151—2165).—α-Ionone (**I**) [semicarbazone, m.p. 142—143° (lit. 137—138°); *δ-phenylsemicarbazone*, m.p. 186·5—187°; 2 : 4-dinitrophenylhydrazone, m.p. 151° (lit. 147—148°)] is readily obtained pure through the H sulphite or oxime. β-Ionone (**II**) is obtained pure by hydrolysis of the semicarbazone (**III**), m.p. 148·5—149°, becomes yellow at >100°, with aq. *o*-$C_6H_4(CO_2H)_2$ in a current of steam; the *δ-phenylsemicarbazone* has m.p. 157·5—158° and is stable to light and air whereas a *phenylsemicarbazone*, m.p. 151—152°, obtained from (**III**) and NH_2Ph at 180°, rapidly becomes yellow in air. The reactions of (**I**), (**II**), and methyl-α-ionone (**IV**) with NaOEt–EtOH and according to Legal, Rosenthaler, Ehrlich–Muller, and Hanriot are described in detail. Reduction of (**I**), (**II**), and (**IV**) with Na in boiling EtOH gives dihydro-α-ionol (**V**), b.p. 126—127°/10 mm. (acetate, b.p. 131—132°/10 mm.), differing in physical consts. from the product of Palfray *et al.* (A., 1937, II, 108), dihydro-β-ionol, b.p. 132—133°/10 mm., m.p. 41° [allophanate, m.p. 162·5—163° (lit. 171·5°); acetate, b.p. 137—138°/10 mm.], and *dihydromethyl-α-ionol*, b.p. 136—138°/10 mm. (*acetate*, b.p. 141—142°/10 mm.), respectively. Hydrogenation (PtO_2 in 90% AcOH at 70°) of (**V**) affords cis-*tetrahydroionol*, b.p. 130—131°/10 mm. (*allophanate*, m.p. 162—162·5°), oxidised to cis-*tetrahydroionone* (*semicarbazone*, m.p. 183—184°; 2 : 4-*dinitrophenylhydrazone*, m.p. 120—120·5°). It is probable that the product obtained by Kandel (A., 1939, II, 169) is the *trans*-isomeride. α-*Methyltetrahydroionol*, b.p. 138—139°/10 mm., is similarly obtained. (**I**) is hydrogenated (Raney Ni in 95% EtOH at 65°) to dihydro-α-ionone, b.p. 119—120°/10 mm. [semicarbazone, m.p. 167—167·5° (lit. 171—172°)]. The dihydroionol obtained by hydrogenation (Raney Ni in 95% EtOH at 65°) is non-homogeneous and appears to contain ~22% of ketones. (**I**) is dehydrated by I to 1 : 1 : 6-trimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene, b.p. 107—108°/10 mm.; under like conditions (**IV**) gives the 1 : 1 : 6 : 7-Me_4-compound, b.p. 120—122°/10 mm. Parachors, mol. surface energies, and dipole moments of the ionones and the corresponding alcohols indicate that the former possess a *cis*-ethylenic structure and that the butenyl or Bu chain is coiled into an open ring. M.p. are corr. H. W.

Reaction between quinones and metallic enolates. XVIII. Mechanisms. L. I. Smith, R. T. Arnold, and J. Nichols (*J. Amer. Chem. Soc.*, 1943, **65**, 2131—2134; cf. A., 1944, II, 54).—The varying modes of reaction of bromopolymethylbenzoquinones with $CHNa(CO_2Et)_2$ or other anionoid reagents are correlated and shown to be rational on the basis of possible modes of resonance. Similar explanations can be applied also outside this series of compounds. R. S. C.

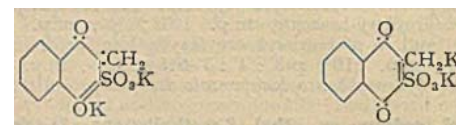
Vitamin-*K* group. I. Synthesis of potassium 2-methyl-1 : 4-naphthaquinone-3-sulphonate. D. A. Bochvar, L. A. Schukina, A. S. Chernyshev, N. G. Semenov, and M. M. Shemiakin. **II. Mechanism of biological action of vitamin-*K* and of its synthetic analogues.** M. M. Shemiakin, L. A. Schukina, and J. B. Shvezov (*J. Amer. Chem. Soc.*, 1943, **65**, 2162—2164, 2164—2167).—I. With $KHSO_3$ in 5% H_2SO_4 and then $K_2Cr_2O_7$, 1 : 2 : 4-O:$C_{10}H_5$Me:O



(III.) (IV.) (V.)

(**I**) gives >9% of K 2-methyl-1 : 4-naphthaquinone-3-sulphonate (**II**) (cf. Fieser and Fieser, A., 1935, 585; Moore, A., 1941, II, 369). By use of aq. $KHSO_3$ (no acid) at 115—120° and then $K_2Cr_2O_7$ or, better, aq. Cl_2 ~60% of (**II**) is obtained. The reaction mechanism is (**I**) ⟶ (**III**) ⟷ (**IV**) ⟷ (**V**) and thence, by oxidation, (**II**). The change (**IV**) → (**V**) is accelerated by H^+ or OH^-, but for (**I**) the reverse change to (**I**) is accelerated by H^+ to a greater degree so that the total effect of acid is unfavourable; for 1 : 4-O:$C_{10}H_6$:O (**VI**) the total effect is favourable (cf. *loc. cit.*). (**II**) has only slightly less antihæmorrhagic effect than has (**I**) (cf. Moore, *loc. cit.*; Baker *et al.*, A., 1942, II, 285; Menotti, A., 1943, II, 303; a different method of test is used).

II. Biological activity of (**I**) and its derivatives is held to be due to biological degradation to *o*-$C_6H_4(CO_2H)_2$ (**VII**) or its derivatives. (**VII**) and particularly its Et_2 ester and diamide have vitamin-*K* activity. In boiling H_2O (30 hr.) (**I**) (20 g.) gives (**VII**) (0·9 g. isolated as anhydride) and a (?) quinhydrone, m.p. >350°; 1·2 g. of (**VII**) is obtained by boiling aq. KOH (45 min.). In H_2O (5 hr.), (**II**) (20 g.) gives 0·8 g. of (**VII**) and 3·3 g. of a *quinhydrone* (**VIII**), m.p. 243—244° (decomp.) (oxidised to a quinone by Cl_2 and reduced to a quinol by Zn–AcOH). In 25% aq. KOH at room temp., (**II**) gives the yellow K_2 salt (**IX**), which in H_2O rapidly gives (**VII**) and (**VIII**) but by further treatment with 25% KOH gives the orange-red K_2 salt (**X**) and thence, by acid, regenerates (**II**). Generation of

(IX.)  (X.)

(**VII**) depends on formation of a 2-CHR: derivative, which explains why (**I**), but no other 2-alkyl derivatives, is antihæmorrhagic and why substitution at $C_{(3)}$ usually has little effect. R. S. C.

Perylene and its derivatives. L. A. Zinke, H. Troger, and E. Ziegler (*Ber.*, 1940, **73**, [*B*], 1042—1048; cf. A., 1937, II, 142).—Contrary to Zinke *et al.* (A., 1927, 1190), perylene (**I**), *o*-$C_6H_4(CO)_2O$, and $AlCl_3$ (or $AlCl_3$–NaCl) at 170° give *di-o-carboxybenzoylperylene*-A_1, m.p. >360°, and -A_3, sinters from 260°, m.p. 292—296°, *o-carboxybenzoylperylene*-A_2, m.p. 277—278° (sinters 260°), and *diphthaloylperylene*-B_1 (violet-blue vat) and -B_2 (blue-green vat). In boiling $PhNO_2$, -A_3 gives -B_1 and ? a half-cyclised acid; gives similarly ? impure -B_2. $(CH_2{\cdot}COCl)_2$, (**I**), and $AlCl_3$ in CS_2 give *γ-keto-γ-3-perylenyl-n-butyric acid*, darkens 240°, m.p. 255° (*Br*$_4$-derivative, m.p. 190°; *Me*, m.p. 183°, and *Et* ester, m.p. 168°), converted by Ac_2O into ? 2 : 3-*succinylperylene*. $(CH_2{\cdot}CO)_2O$ and (**I**) give impure products. R. S. C.

IV.—STEROLS AND STEROID SAPOGENINS.

Organ extracts. III. Unsaponifiable lipoids from arteriosclerotic aortas. E. Hardegger, L. Ruzicka, and E. Tagmann (*Helv. Chim. Acta*, 1943, **26**, 2205—2221).—The comminuted material is extracted exhaustively with $COMe_2$ and neutral lipoids result after removal of acids and substances readily sol. in H_2O from the extract. These are hydrolysed successively with $Ba(OH)_2$ and KOH (whereby alterations of the native material are not excluded) and the unsaponified residue is separated into its components by crystallisation and chromatography over Al_2O_3. 370 human aortas yield 127 g. of unsaponifiable matter from which is obtained ~90 g. of cholesterol (**I**) containing (according to $[\alpha]_D$) ~5·6% of dihydrocholesterol. On average 1 aorta contains ~240 mg. of total (**I**) compared with 5—50 mg. in the normal organ. From the residual (**I**)-poor unsaponifiable matter are isolated: $\Delta^{3:5}$-cholestadien-7-one (**II**), m.p. 114—114·5°, $[\alpha]_D$ −299°±5° in $CHCl_3$ (*oxime*, m.p. 176—178°; *semicarbazone*, m.p. 206·5—207·5°); $\Delta^{4:6}$-cholestadien-3-one (**III**), m.p. 79·5—81°, $[\alpha]_D$ +35°±2° in $CHCl_3$ (oxime, m.p. 176—177°); *cholestane*-3(β) : 5 : 6(trans)-*triol* (**IV**), m.p. 244—245° (softens at 227°) (diacetate, m.p. 165—167°), which does not give a colour reaction with $SbCl_3$, $C(NO_2)_4$, or $CCl_3{\cdot}CO_2H$; 7(β)-hydroxycholesterol (**V**), m.p. 188—188·5°, $[\alpha]_D$ −93°±2° in $CHCl_3$ (*dibenzoate*, m.p. 151·5—152·5°); batyl alcohol; unidentified *substance A*, m.p. 301—303°, $[\alpha]_D$ −61°±17° in $CHCl_3$; *substance B*, m.p. 301—301·5°, $[\alpha]_D$ +25·5°±3° in $CHCl_3$; *substance C*, m.p. 79·5—80°, $[\alpha]_D$ ±0°±1° in $CHCl_3$; *substance D*, m.p. 219—221°, $[\alpha]_D$ −66°±3° in $CHCl_3$, saturated towards $C(NO_2)_4$, which gives a red colour with $SbCl_3$ in $CHCl_3$ and a blue colour with $CCl_3{\cdot}CO_2H$ in $CHCl_3$; *substance E*, m.p. 68—69°, $[\alpha]_D$ +17°±4° in $CHCl_3$, which gives a marked yellow-brown colour with $C(NO_2)_4$. Provisionally, the possibility cannot be excluded that (**II**), (**III**), (**IV**), and (**V**) [with the possible exception of (**II**)] do not exist pre-formed in the aortas but are formed during the working up from (**I**). H. W.

Organ extracts. IV. Unsaponifiable lipoids from swine spleen. V. Prelog, L. Ruzicka, and P. Stein (*Helv. Chim. Acta*, 1943, **26**, 2222—2242).—The material is extracted with $COMe_2$ and the extract is treated with hot MeOH into which the bulk of the unsaponifiable matter passes, leaving the fatty acid glycerides undissolved. From the MeOH extract the bulk of the cholesterol (**I**) is separated by crystallisation from $COMe_2$. What remains is hydro-

lysed by NaOH–MeOH and much of the fatty acids are separated as the insol. Ba salts, which retain a considerable proportion of the residual unsaponifiable matter, the removal of which is described. This is then treated with Girard's reagent *T* and the reacted and unchanged portions are chromatographed over Al_2O_3. The following are isolated: Δ^5-cholestene-3(β) : 7(α)-diol [7(α)-hydroxycholesterol], m.p. 168—170°, $[\alpha]_D^{21}$ −12·3°±3° in $CHCl_3$ (dibenzoate, m.p. 170·5°, $[\alpha]_D^1$ +97°+5° in $CHCl_3$), which does not give a colour with $C(NO_2)_4$ and with $SbCl_3$, $CCl_3{\cdot}CO_2H$, and Lifschütz reagent gives the colours typical of hydroxycholesterols; Δ^4-cholestene-3(β) : 6-diol, m.p. 254°, $[\alpha]_D^{20}$ +8·4°±4° in C_5H_5N (diacetate, m.p. 132—133°, $[\alpha]_D^{20}$ −12°±3° in $CHCl_3$; dibenzoate, m.p. 181°, $[\alpha]_D^{20}$ −73·0°±2·5° in $CHCl_3$); cholestan-3(β)-ol-6-one, m.p. 128—129°, $[\alpha]_D^{18}$ −13·6°±3° in $CHCl_3$; $\Delta^{3,5}$-cholestadien-7-one, m.p. 114°, $[\alpha]_D^{14}$ −305°±4° in $CHCl_3$; $\Delta^{4:6}$-cholestadien-3-one (oxime, m.p. 173·5—175°); *substance*, $C_{27}H_{46}O_2$, m.p. 155·5—156°, $[\alpha]_D^{19}$ −132°±4° in $CHCl_3$, which gives the colour reactions typical of hydroxycholesterols, gives a *monoacetate*, m.p. 110—111°, $[\alpha]_D^{20}$ −118°±4° in $CHCl_3$, and a *monobenzoate*, m.p. 134—135°, $[\alpha]_D^{20}$ −79°±3° in $CHCl_3$, cannot be pptd. with digitonin, and is oxidised by $Al(OPh)_3$ and $COMe_2$ to $\Delta^{4:6}$-cholestadien-3-one (oxime, m.p. 172—174°); in EtOH it does not exhibit absorption in the ultraviolet; it gives a marked depression of m.p. with Δ^6-cholestene-3 : 5-diol, of which it is very possibly a stereoisomeride; batyl alcohol, m.p. 64·5—65·5°, $[\alpha]_D^{21}$ +5·3°±1·5° in $CHCl_3$ (*bisphenylurethane*, m.p. 98·5—99°); (?) palmitylsphingosine, m.p. 90—91°, $[\alpha]_D^1$ ±0°±3° in $CHCl_3$; *compound* A, $C_{27}H_{46-48}O$, m.p. 210—216°, $[\alpha]_D^1$ −74·8°±2° in $CHCl_3$, which does not give a yellow colour with $C(NO_2)_4$; *substance* B, $C_{28}H_{48}O_3$, m.p. 200—201°, $[\alpha]_D^{19}$ −5·7°±3° in $CHCl_3$, which does not give the hydroxycholesterol colour reactions or a yellow colour with $C(NO_2)_4$, does not give a ppt. with digitonin, and is not identical with cholestane-3(β) : 5 : 6-(*trans*)-triol or -3(β) : 5 : 6-(*cis*)-triol; *substance* C, m.p. 86—87°, which does not give a yellow colour with $C(NO_2)_4$. As impurities a hydrocarbon, $C_{25}H_{52}$, m.p. 53·5—54°, and friedelin, m.p. 255—259°, are isolated. According to their constitution, all the isolated steroids can be represented as oxidation or transformation products of (**I**). In this and similar researches it has been found possible to isolate from organ extracts all derivatives of (**I**) which have been identified from the autoxidation or photo-oxidation of (**I**). It cannot therefore be decided definitely whether the transformation products of (**I**) isolated from organ extracts are present as such in the organism or are produced during the working up. The biochemical significance of the isolation of the steroids is therefore very difficult to evaluate. The total result is, however, valuable. Since steroids with 18, 19, and 21 C atoms have only so far been isolated from the sexual tract, the adrenals, and urine, their occurrence appears provisionally to be characteristic of these sources. M.p. are corr. H. W.

Steroids and sex hormones. LXXXVIII. 3(α)-Hydroxy*allo*ætiocholanic acid. P. A. Plattner and A. Fürst (*Helv. Chim. Acta*, 1943, **26**, 2266—2273).—Oxidation of 3(β)-hydroxy*allo*ætiocholanic acid by CrO_3 in AcOH gives 3-keto*allo*ætiocholanic acid (**I**), m.p. 260—262°, the yield of which is greatly diminished by the simultaneous formation of *isoallo*ætiolithobilianic acid. Similar oxidation of the hydrogenation product of $\Delta^{5:6}$-3(β)-hydroxypregnen-20-one gives 20-*keto*-23-allo*pregnane*-2 : 3-*diacid*, m.p. 219—219·5°, $[\alpha]_D$ +93·8° in $CHCl_3$. Hydrogenation (PtO_2 in AcOH containing HBr at 60°) of (**I**) gives 3(α)-*acetoxy*allo*ætiocholanic acid*, m.p. 215—218°, $[\alpha]_D$ +50·3° in $CHCl_3$; the *Me* ester (**II**), m.p. 199—202°, $[\alpha]_D$ +54·5° in $CHCl_3$, is hydrolysed to 3(α)-*hydroxy*allo*ætiocholanic acid* (**III**), m.p. 281—284°, $[\alpha]_D$ +45·3° in $CHCl_3$ (*Me* ester, m.p. 178—181°, $[\alpha]_D$ +52·6° in $CHCl_3$). Similar hydrogenation of larger quantities of crude (**I**) gives a product from which cryst. derivatives of (**III**) cannot be separated. From the ethereal solution of the hydrogenated product separates a substance of high m.p. from which by esterification (CH_2N_2) and chromatography *Me*$_2$ isoallo*ætiolithobilianate*, m.p. 82—83°, $[\alpha]_D$ +47·2° in $CHCl_3$, is isolated. Esterification and acetylation of the more sol. products lead to *Me* allo*ætiocholanate*, m.p. 140—142°, $[\alpha]_D$ +55·4° in $CHCl_3$ (*acid*, m.p. 225—227°, $[\alpha]_D$ +55·8° in $CHCl_3$), and *Me* 3(β)-*bromo*allo*ætiocholanate*, m.p. 135°, $[\alpha]_D$ +59·3° in $CHCl_3$. Me 3(β)-hydroxy- is converted by PBr_3 in boiling C_6H_6 into *Me* 3(α)-*bromo*allo*ætiocholanate*, m.p. 160°, $[\alpha]_D$ +69·8° in $CHCl_3$. *Me* 3(β)-p-*toluenesulphonyloxy*allo*ætiocholanate*, m.p. 147°, $[\alpha]_D$ +80·1° in $CHCl_3$, from the OH-ester and *p*-$C_6H_4Me{\cdot}SO_2Cl$ in dry C_5H_5N at 0° and then at room temp., is converted by anhyd. NaOAc in boiling AcOH into (**II**) (yield 50%) and *Me* $\Delta^{2:3}$- or $\Delta^{3:4}$-allo*ætiocholenate*, m.p. 129—131°, $[\alpha]_D$ +94·8° in $CHCl_3$, hydrogenated (PtO_2 in AcOH) to Me allo*æt*iocholanate, m.p. 142—144·5°, $[\alpha]_D$ +53·3° in $CHCl_3$. M.p. are corr. H. W.

Bile acids and related substances. XXVIII. 12(α)-Hydroxycholanic acid. M. Sorkin and T. Reichstein (*Helv. Chim. Acta*, 1943, **26**, 2097—2101; cf., A., 1942, II, 412).—Hydrogenation (Raney Ni–MeOH at 20°) of Me 12-ketocholanate (**I**) gives a mixture of Me 12(α)- (**II**) and 12(β)- (**III**) -hydroxycholanate, partly separated chromatographically, after which (**III**) can be caused to crystallise. Crude (**II**) is hydrolysed to 12(α)-*hydroxycholanic acid* (**IV**), m.p. 109—115°, $[\alpha]_D^{12}$ +37·9°±2° in $COMe_2$, also obtained by treating Me 3-keto-12(α)-acetoxycholanate with $N_2H_4{\cdot}H_2O$ and NaOEt–EtOH at 180°. 12(β)-Hydroxycholanic acid has $[\alpha]_D^{12}$ +43·5°±2° in $COMe_2$. The constitution of (**IV**) is established by methylation (CH_2N_2) followed by oxidation (CrO_3 in AcOH at room temp.) to (**I**). Substitution of NaOH–MeOH for pure MeOH in the hydrogenation of Me 3(α)-hydroxy-12-ketocholanate so favours the production of 3(α) : 12(α)-dihydroxycholanic acid that the greater part of it can be separated pure by two crystallisations; a simplified method is described for the separation of the remainder of it from deoxycholic acid. M.p. are corr. (block); limit of error ±2°. H. W.

Steroids and sex hormones. LXXXIX. Simple digitaloid lactones with *allo*cholane configuration. P. A. Plattner, L. Ruzicka, and A. Fürst (*Helv. Chim. Acta*, 1943, **26**, 2274—2278).—3(α)-Acetoxy-*allo*ætiocholanic acid is converted by $SOCl_2$ in boiling C_6H_6 into the chloride, which with CH_2N_2 in C_6H_6–Et_2O at −10° affords 21-*diazo*-3(α)-*acetoxy*allo*pregnan*-20-*one*, decomp. 156—158°, $[\alpha]_D$ +141·6° in $CHCl_3$, converted by AcOH at 100° into 3(α) : 21-*diacetoxy*allo*pregnan*-20-*one*, m.p. 165°, $[\alpha]_D$ −92·1° in $CHCl_3$. This is converted by Zn and $CH_2Br{\cdot}CO_2Et$ in C_6H_6–dioxan followed by treatment with boiling dil. HCl and Ac_2O–C_5H_5N at room temp. into 20 : 21-*dihydroxy*-3(α)-*acetoxyno*rallo*cholanolactone* (**I**), m.p. 255° (loss of H_2O), $[\alpha]_D$ +56° in $CHCl_3$. (**I**) is converted by prolonged boiling with Ac_2O into $\Delta^{-0:22}$-21-*hydroxy*-3(α)-*acetoxy*-, m.p. 230°, $[\alpha]_D$ +19° in $CHCl_3$, and thence by 2N-HCl in dioxan at 100° into $\Delta^{20:22}$-3(α) : 21-*dihydroxy*-, m.p. 243—244° $[\alpha]_D$ +10° in $CHCl_3$, -*no*rallo*cholenolactone*. 3(β)-Acetoxy*allo*ætiocholanic acid similarly gives 21-diazo-3(β)-acetoxy*allo*pregnan-20-one, m.p. 131—132°, $[\alpha]_D$ +134·4° in $CHCl_3$, which gives 3(β) : 21-diacetoxy*allo*pregnan-20-one, m.p. 151—152·5°, $[\alpha]_D$ +80·8° in $CHCl_3$, converted into $\Delta^{20:22}$-21-*hydroxy*-3(β)-*acetoxyno*rallo*cholenolactone*, m.p. 193—194°, $[\alpha]_D$ +1° in $CHCl_3$. Likewise *allo*ætiocholanic acid yields 21-*diazo*allo*pregnan*-20-*one*, m.p. 120—121° (decomp.), $[\alpha]_D$ +151·3° in $CHCl_3$, which gives successively 21-*acetoxy*allo*pregnan*-20-*one*, m.p. 200°, $[\alpha]_D$ +101·8° in $CHCl_3$, and $\Delta^{-0:22}$-21-*hydroxyno*rallo*cholenolactone*, m.p. 170°, $[\alpha]_D$ +1·3° in $CHCl_3$. M.p. are corr. H. W.

Constituents of the adrenal cortex and related substances. Ætiocholane-3(α) : 12(β)-diol-17-one. H. Reich and T. Reichstein (*Helv. Chim. Acta*, 1943, **26**, 2102—2109).—Me 3(α) : 12(β)-diacetoxycholanate is oxidised by CrO_3 in AcOH at ~75° and the product is divided into acidic (**I**) and neutral (**II**) portions. Direct crystallisation of (**II**) leads to the removal of unchanged material and the residue is hydrolysed by alkali. The acids thus isolated contain some deoxycholic acid and a *lactone*, $C_{25}H_{38}O_5$, m.p. 285—288°, which is probably a monoacetate corresponding to the lactone obtained by Miescher *et al.* (A., 1939, II, 160) by the oxidation of cholesteryl acetate dibromide and is converted by energetic acetylation into a *diacetate*, $C_{27}H_{40}O_6$, m.p. 271—274°. The relatively small amounts of neutral, unsaponifiable substances are treated with Girard's reagent *T*, thus leading to the isolation of pregnane-3(α) : 12(β)-diol-20-one (identified as the diacetate) and ætiocholane-3(α) : 12(β)-diol-17-one (*diacetate*, m.p. 162—162·5°, $[\alpha]_D^{16}$ +176·0°±2°, $[\alpha]_{5461}^{16}$ +213·7°±2° in $COMe_2$). (**I**) is completely hydrolysed, methylated (CH_2N_2), and fractionally hydrolysed whereby Me 3(α) : 12(β)-diacetoxyætiocholanate is largely unaffected. All the yields are very poor. M.p. are corr. (block); limits of error ±2°. H. W.

D-Homosteroids.—See B., 1944, III, 33, 34.

V.—TERPENES AND TRITERPENOID SAPOGENINS.

Characterisation of carboxylic acids by carbodi-imides. X. Optically active carbodi-imides. F. Zetzsche and A. Fredrich (*Ber.*, 1940, **73**, [*B*), 1114—1123).—*l*-Menthylamine (**I**) and CS_2 in PhMe at ~50° and then the b.p. give 83% of *s*-di-*l*-menthylthiocarbamide, m.p. 201°, $[\alpha]_D$ −125·6° in $CHCl_3$ (in this and other cases), converted by HgO in CS_2 at room temp. into *carbodi*-l-*menthylimide*, $C(:NR)_2$ (82%), b.p. 213—215°/14 mm., $[\alpha]_D$ −101·4°, which gives no ureides. *p*-$NMe_2{\cdot}C_6H_4{\cdot}NCS$ (**II**) and (**I**) in Et_2O at room temp. give N-p-*dimethylaminophenyl*-N′-l-*menthylthiocarbamide* (87%), m.p. 149—150°, $[\alpha]_D$ −80·3°, and thence N-p-*dimethylaminophenyl*-N′-l-*menthylcarbodi-imide* (**III**) (67%), m.p. 50—52°, $[\alpha]_D$ −70·3°. With HCO_2H in Et_2O, (**III**) gives N-p-*dimethylaminophenyl*-N′-l-*menthylcarbamide*, m.p. 229—230°, $[\alpha]_D$ −62·9°, and with stearic acid in C_5H_5N at 100° or, in other cases, RCO_2H in Et_2O at room temp. gives N-*stearoyl*-, m.p. 115—116°, $[\alpha]_D$ −33·2°, N-*benzoyl*-, m.p. 115—116°, $[\alpha]_D$ −55·0°, N-p-*bromobenzoyl*-, m.p. 216—218°, $[\alpha]_D$ −48·8°, N-*cinnamoyl*- m.p. 148—149°, $[\alpha]_D$ −59·7°, and N-*piperoyl*-N- (or N′-)p-*dimethylaminophenyl*-N′- (or N-)l-*menthylcarbamide*, m.p. 190—192°. Bornylamine hydrochloride (**IV**), $[\alpha]_D$ −5·3°, gives similarly *s*-dibornylthiocarbamide (55%), sinters 225°, m.p. 227—228°, $[\alpha]_D$ −19·4°, and thence *carbodibornylimide* (84%), m.p. 229—231°, which gives N-*benzoyl*-NN′-*dibornylcarbamide*, sinters 148°, m.p. 150—152° (but no other urcide), and with AcOH or $H_2C_2O_4$ in dioxan gives dibornylcarbamide, sublimes from 300°, decomp. ~345° (lit. sublimes >290°). The base from (**IV**)

with (**II**) gives N-p-*dimethylaminophenyl*-N'-*bornylthiocarbamide*, m.p. 181°, $[\alpha]_D$ −11·1°, and thence the *carbodi-imide*, m.p. 31—34°, b.p. 203—204°/0·12 mm., $[\alpha]_D$ −11·9°, which yields, as above, N-p-*dimethylaminophenyl*-N'-*bornylcarbamide*, m.p. 199—200°, and the *CHMeBr·CO*, m.p. 139—140°, *Bz*, m.p. 137—138°, and *cinnamoyl* derivatives, m.p. 139—140°, thereof. *s*-Di*cyclo*hexylthiocarbamide, m.p. 180—181°, is obtained in 95·8% yield from the base and CS_2 in PhMe. N'-cyclo*Hexyl*-N-p-*dimethylaminophenylthiocarbamide* (prep. as above; 92% yield), m.p. 131—132°, gives the *carbodi-imide*, b.p. 175—176°/0·6 mm., *carbamide* (**VI**), m.p. 187—188°, and the *crotonyl*, m.p. 107—108°, *stearoyl*, m.p. 80—81°, *CHMeBr·CO*, m.p. 138—139°, *CHEtBr·CO*, m.p. 120—121°, *Bz*, sinters 140°, m.p. 141—142°, and *cinnamoyl* derivative, m.p. 160—161°, thereof. Similarly are prepared $CS(NH{\cdot}CH_2Ph)_2$ (95·4% yield) and *carbodibenzylimide* (**VII**) (76%), b.p. 208—210°/18 mm., which is unstable and gives a *dimer*, m.p. 102—103° [reacts more slowly than does (**VII**)]. In C_5H_5N at 100° (**VII**) with BzOH gives *benzoyl*-NN'-*dibenzylcarbamide*, m.p. 98—99°, but with AcOH or *n*-$C_5H_{11}{\cdot}CO_2H$ gives $CO(NH{\cdot}CH_2Ph)_2$, m.p. 166—167°. N-p-*Dimethylaminophenyl*-N'-*benzylthiocarbamide* has m.p. 127—128°. With $CH_2{:}CH{\cdot}CO_2H$, α-bromopalmitic acid, or $CHMeBr{\cdot}CH_2{\cdot}CO_2H$, (**V**) gives only (**VI**). No ureide is obtained from (**III**) by $CHMeBr{\cdot}CO_2H$, $CHEtBr{\cdot}CO_2H$, $C_{14}H_{29}{\cdot}CHBr{\cdot}CO_2H$, or $CHMeBr{\cdot}CH_2{\cdot}CO_2H$. Formation of ureides thus depends on the nature of both the acid and carbodi-imide (cf. C., 1944, Part 2). R. S. C.

ω-Nitrocamphene. P. Lipp, H. Braucker, and H. Sauer [with, in part, J. Gerdes] (*Ber.*, 1940, **73**, [*B*], 1146—1150; cf. A., 1940, II, 136).—Reduction of ω-nitrocamphene (**I**) with Zn dust and AcOH gives mainly tricyclal (**II**) containing a small proportion of camphenilanealdehyde, separated from (**II**) as its enol acetate and identified by oxidation to *iso*camphenilanic acid (**III**), m.p. 117·5—118·5° (corr.). In addition to (**II**) and in the ratio ~3 : 1 there is produced 2-acetoxy*apo*camphanealdehyde [*semicarbazone*, m.p. 216·5—217·5° (corr.)], readily converted by air and more readily by other oxidising agents into 2-acetoxy*apo*camphanecarboxylic acid, m.p. 121—122° (corr.) [corresponding *chloride*, b.p. 111—113°/0·3 mm., m.p. ~60°, and *amide*, m.p. 99—100° (corr.)]. This is hydrolysed to 2-hydroxy*apo*camphanecarboxylic acid, m.p. 225—226° (lit. m.p. 237°), which is oxidised ($KMnO_4$–KOH) to ketopinic acid, m.p. 232·5—234° (corr.). The non-carboxylic compounds contain essentially the two *iso*camphanols, removed as the *p*-nitrobenzoates, which are only partly separable from one another by crystallisation (small amounts of a p-*nitrobenzoate*, m.p. 148—149°, are isolated); the alcohols from the remaining mixture of *p*-nitrobenzoates are oxidised to (**III**). The nitrile, b.p. 93·5—96°/8 mm., of (**III**) or camphenilanic acid is indifferent towards *p*-$NO_2{\cdot}C_6H_4{\cdot}COCl$. In contrast to the complete change in system caused by additions to (**I**) in strongly acid solution the *iso*camphane skeleton is changed only in part and in part remains intact in a slightly acid medium. H. W.

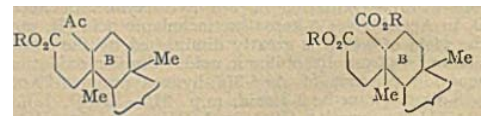
Rearrangement of camphorquinone. I. Formation and reactions of the inactive modifications of 2 : 2 : 3-trimethyl*cyclo*hexan-4-one-1-carboxylic acid. R. N. Chakravarti (*J. Indian Chem. Soc.*, 1943, **20**, 301—306).—Synthetic camphor is oxidised with SeO_2 to *dl*-camphorquinone (cf. Evans *et al.*, A., 1934, 299), which with conc. H_2SO_4 gives dl-2 : 2 : 3-*trimethyl*cyclo*hexan*-4-*one*-1-*carboxylic acid* (**I**), m.p. 109° (cf. *d*-acid, Manasse and Samuel, A., 1898, i, 147; 1903, i, 45; Bhagvat and Simonsen, A., 1927, 250) [*monohydrate*, m.p. 73—74°; *semicarbazone*, m.p. 230—231°; *Me* ester, b.p. 100°/4 mm.; *Et* ester (**II**), b.p. 120°/6 mm.]. Clemmensen reduction of (**I**) gives 1 : 2 : 2-*trimethyl*cyclo*hexane*-3-*carboxylic acid*, b.p. 118°/5 mm. (p-*phenylphenacyl ester*, m.p. 114°), the *Me* ester, b.p. 95°/12 mm., of which when dehydrogenated by Se at 340° in a sealed tube for 28 hr. gives *o*-xylene and *o*-xylene-3-carboxylic acid. Treatment of (**II**) with $Et_2C_2O_4$ and NaOEt gives an oxalyl derivative, which loses CO on heating to yield *Et*$_2$ 2 : 3 : 3-*trimethyl*cyclo*hexan*-1-*one*-4 : 6-*dicarboxylate* (**III**), b.p. 155°/6 mm. (violet colour with $FeCl_3$–EtOH), which in a closed tube with NaOEt at 150—200° for 24 hr. gives *Et*$_3$ αββ-*trimethylpentane*-αγε-*tricarboxylate*, b.p. 160°/4 mm. (no colour with $FeCl_3$–EtOH). Treatment of this with Na and C_6H_6 regenerates (**III**), hydrolysis of which with either KOH–H_2O–EtOH or dil. HCl re-forms (**I**). S. A. M.

New derivatives of 4-phenylcamphor. S. S. Nametkin and T. V. Scheremeteva (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, **38**, 131—134).—4-Phenyl- (**I**) and 4-*p*-aminophenyl-camphor (**II**) (*Ac* derivative, m.p. 181—184°) are prepared by modified methods. (**I**) and 100% H_2SO_4 at 35—40° give 4-p-*sulphophenylcamphor*, m.p. 189—190° (*Ba*, +6H_2O, and *Pb* salt, +8H_2O). 4-p-*Hydroxyphenylcamphor*, m.p. 125°, is obtained by decomp. of the aq. diazonium solution from (**II**) at room temp. (**I**) and $HCO_2C_5H_{11}$-*iso* + Na yield 4-*phenyl*-3-*hydroxymethylenecamphor* (**III**), m.p. 50—54° (*Bz* derivative, m.p. 149—150°), converted by prolonged action of aq. AcOH at room temp. into 3-*aldehydo*-4-*phenylcamphor*, m.p. 91—95° (does not give a Bz derivative). 4-Phenylcamphorquinone, m.p. 142—143°, is obtained from (**III**) and 1% $KMnO_4$ in cold dil. alkali, and 4-*p*-nitrophenylcamphor and SeO_2–Ac_2O afford 4-p-*nitrophenylcamphorquinone*, m.p. 137°. A. T. P.

A tricyclic compound obtained by the di-inene double-addition reaction.—See A., 1944, II, 101.

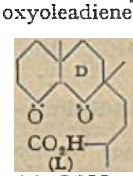
Triterpenes. LXXXII. Degradation of diacetoxynorlupanone and acetylbetulic acid to acetoxybisnorlupandicarboxylic acid. L. Ruzicka and E. Ray (*Helv. Chim. Acta*, 1943, **26**, 2143—2151).—Diacetoxynorlupanone (A., 1941, II, 71) in C_5H_5 is partly hydrolysed by KOH–EtOH at room temp. to *dihydroxynorlupanone* 2-*acetate*, m.p. 293°, $[\alpha]_D$ −7°, oxidised by CrO_3 in AcOH at room temp. to *acetoxynorlupanonic acid* (**I**), m.p. 253°, $[\alpha]_D$ −10°. The corresponding *Me* ester (**II**), m.p. 235°, $[\alpha]_D$ −16°, is partly hydrolysed to Me norlupanolonate, m.p. 253°, $[\alpha]_D$ −45°, identical with the product obtained by Ruzicka *et al.* (A., 1941, II, 72) by the oxidation of Me acetylbetulate, the constitution of which is thereby established. (**I**) is hydrogenated (PtO_2 in AcOH) to *acetylnorlupandiolic acid*, m.p. 289°, $[\alpha]_D$ +10°, which could not be lactonised. (**II**) is oxidised by SeO_2 in hot AcOH to *Me acetoxynorluponalonate*, m.p. 184°, $[\alpha]_D$ −16°, further oxidised by 30% H_2O_2 in boiling AcOH and then esterified to *Me acetoxybisnorlupandicarboxylate* (**III**), m.p. 182°, $[\alpha]_D$ −13°. Acetylbetulic acid is oxidised by SeO_2 in boiling AcOH to *acetyl-lupenalolic acid*, m.p. 295°, $[\alpha]_D$ +11°, which does not give a yellow colour with $C(NO_2)_4$ and yields a yellow solution in conc. H_2SO_4 which rapidly becomes red. It is oxidised by CrO_3 in AcOH to *acetylbisnorlupanoldicarboxylic anhydride*, m.p. 352°, $[\alpha]_D$ +32°, *acetyl-lupenoldicarboxylic acid*, m.p. ~300°, $[\alpha]_D$ +14°, which does not give a colour reaction with $C(NO_2)_4$, and (after esterification) (**III**). Hydrolysis of (**III**) by KOH–MeOH gives *Me*$_2$ *hydroxybisnorlupandicarboxylate*, m.p. 210°, $[\alpha]_D$ −13°, and the corresponding *Me*$_1$ ester, m.p. 296°. M.p. are corr. $[\alpha]_D$ are in $CHCl_3$ (*l* = 1). The experiments further confirm the presence of the *iso*propenyl group in the C skeleton of betulin. The formulation of lupane derivatives by Jones *et al.* (A., 1942, II, 60) and Kon *et al.* (*ibid.* 60) is criticised adversely. H. W.

Triterpenes. LXXXIII. Oxidative degradation of rings A and B in hederagenin. L. Ruzicka, J. Norymberski, and O. Jeger (*Helv. Chim. Acta*, 1943, **26**, 2242—2250).—Repetition of the work of Kitasato *et al.* (A., 1932, 1035; 1933, 612) confirms the composition of the hydroxytetracarboxylolactone Me_3 ester $C_{30}H_{46}O_8$ (**I**) and thus brings indirect evidence of the attachment of $C_{(30)}$ of the oleanolic acid skeleton to C of the ring. Hederagenin is converted by 33% HBr–AcOH into diacetylhederageninlactone, m.p. 248—248·5°, hydrolysed by KOH–EtOH to hederageninlactone (**II**), m.p. 358—360° (high vac.). Hederageninbromolactone is oxidised by CrO_3 in AcOH containing a little conc. H_2SO_4 to (?) hedragonebromolactone and acidic products, debrominated (Zn dust in AcOH) and then converted by HBr–AcOH into hedragenone dicarboxylolactone, m.p. 266—267°, $[\alpha]_D$ +23·7° (Me ester, m.p. 199—200°, $[\alpha]_D$ +28·5°). (**II**) is oxidised by CrO_3 in boiling AcOH to hedragonclactone, m.p. 309—310° (vac.), $[\alpha]_D$ +44·0, and the ketohydroxydicarboxylolactone (**III**) (*A*; R = H), m.p. 263—264°. The corresponding Me ester is oxidised by CrO_3 and H_2SO_4–AcOH and

(*A.*)  (*B.*)

the product is dissolved in Et_2O which is extracted successively with aq. $KHCO_3$ and Na_2CO_3. The former extract gives (**III**), sparingly sol. in Et_2O, and the hydroxycarboxylolactone (*B*; R = H), m.p. 238—239°, converted by CH_2N_2 in Et_2O–$CHCl_3$ into the *Me*$_2$ ester, m.p. 170—170·5°, and passing when heated at 240—250°/high vac. into the *pyroketone*, $C_{27}H_{40}O_3$, m.p. 288—289° (high vac.), $[\alpha]_D$ +152°. The portion of the $KHCO_3$ extract which is freely sol. in Et_2O after esterification with CH_2N_2 affords (**I**), m.p. 199—200°, $[\alpha]_D$ −16·6°. The Na_2CO_3 extract yields (**III**). M.p. are corr. $[\alpha]_D$ are in $CHCl_3$. H. W.

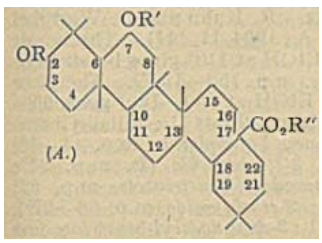
Triterpenes. LXXXIV. New evidence of the different position of the carboxyl group in oleanolic and glycyrrhetic acid. L. Ruzicka, O. Jeger, and W. Ingold (*Helv. Chim. Acta*, 1943, **26**, 2278—2282).—Energetic oxidation of oleanolic and deoxoglycyrrhetic acid with SeO_2 gives dienedione derivatives converted by CrO_3 into oxides, which when treated drastically with alkali suffer fission of ring E with production of different acids. This behaviour is not compatible with the formulation of Kon *et al.* (A., 1942, II, 148, 418), according to which only one acid should be produced. Me $\Delta^{10:11\cdot13:18}$-2-acetoxyoleadiene-12 : 19-dione-20-carboxylate is oxidised by CrO_3 in AcOH at 90° and then at room temp. to *Me* $\Delta^{10:11}$-13 : 18-*oxido*-2-*acetoxyoleanene*-12 : 19-*dione*-20-*carboxylate*, m.p. 282—283°, $[\alpha]_D$ +86° in $CHCl_3$, which is transformed by 10% KOH at 200° into the *nor-acid* (**I**), m.p. 241°, $[\alpha]_D$ +101° in C_5H_5N, +131° in $COMe_2$ (non-cryst. *Me* ester), which gives a marked enol reaction with $FeCl_3$ in EtOH and a yellow colour with $C(NO_2)_4$. M.p. are corr. H. W.



(I.)

Triterpenes. LXXXV. Sumaresinolic acid. L. Ruzicka, O. Jeger, A. Grob, and H. Hösli (*Helv. Chim. Acta*, 1943, **26**, 2283—

2300).—Sumaresinolic acid (**I**) belongs to the oleanolic acid (**II**) group and, like hederagenin, siaresinolic and echinocystic acid, to the sub-group of hydroxyoleanolic acids. The position of 1 OH in (**I**) is not definitely assigned but it must be attached to $C_{(7)}$ or $C_{(8)}$ in ring B. In formula *A* (R = R′ = R″ = H) OH is placed arbitrarily at $C_{(7)}$; $C_{(8)}$ cannot be excluded. In the following formulæ *x* indicates 7 or 8. The relationship of (**I**) to (**II**) is established by chemical reactions and comparison of $[\alpha]_D$ for analogous derivatives of the acids. Extraction of Sumatra gum benzoin with boiling EtOH and treatment of the extract with NaOH leads through the Na salt (**III**) to (**I**), m.p. 298°, $[\alpha]_D$ +54·0°, converted by CH_2N_2 in Et_2O at 0° into the Me ester (**IV**), m.p. 220—221°, $[\alpha]_D$ +46·7°, also obtained from (**III**) and Me_2SO_4 and hydrolysed with great difficulty (Claisen solution at 200° for 12 hr.) to (**I**). The Et ester has m.p. 212°, $[\alpha]_D$ +44·7°. (**IV**) is transformed by Ac_2O in C_5H_5N at room temp. into *Me* 2-*acetylsumaresinolate* (**V**), m.p. 227°, $[\alpha]_D$ +40·6°, converted by mild alkaline hydrolysis into (**IV**). *Et* 2-*acetylsumaresinolate* has m.p. 231°. Passage of HCl into a solution of (**V**) in AcOH at room temp. affords *Me* 2-*acetylanhydrosumaresinolate*, m.p. 174—175°, $[\alpha]_D$ +48°, obtained analogously but in poorer yield from (**IV**). *Me diacetylsumaresinolate* (**VI**), m.p. 258°, $[\alpha]_D$ +25·3°, is obtained from HCl, Ac_2O, and (**V**) at 100° and subsequently at room temp. or from (**V**) and BF_3–Et_2O in Ac_2O at room temp. Mild hydrolysis converts (**VI**) into *Me* x-*acetylsumaresinolate*, m.p. 134—136° (loss of MeOH of crystallisation and softening ~100°), $[\alpha]_D$ +48·0°, reacetylated by Ac_2O in C_5H_5N at room temp. to (**VI**) and drastically hydrolysed to (**IV**). (**I**) is oxidised by CrO_3 in AcOH at room temp. to $\Delta^{12:13}$-x-*keto*-2-*hydroxyoleanene*-28-*carboxylic acid* (**VII**), m.p. 286—287°, $[\alpha]_D$ +31·6°, converted by Ac_2O in C_5H_5N into a mixed *anhydride*, $C_{34}H_{50}O_7$, m.p. 312°, of the ketoacetoxy-acid and AcOH, which is well adapted to the isolation of homogeneous (**VI**). *Me* $\Delta^{12.13}$-x-*keto*-2-*hydroxysumaresenecarboxylate* (**VIII**), m.p. 205—206°, is obtained analogously from (**IV**) or from (**VI**) and CH_2N_2. (**V**) is oxidised by CrO_3 to *Me* $\Delta^{12:13}$-x-*keto*-2-*acetoxyoleanene*-28-*carboxylate* (**IX**), m.p. 285—286°, $[\alpha]_D$ +44·9°, converted by mild hydrolysis into (**VIII**), which is reacetylated to (**IX**) and by drastic hydrolysis gives (**VII**). It appears to be unchanged by N_2H_4,H_2O and NaOEt–EtOH at 210—220° but is quantitatively reduced (Clemmensen) to the 13 : 28-*lactone* of x-*keto*-13-*hydroxy*-2-*acetoxyoleanane*-28-*carboxylic acid* (**X**), m.p. 324—326° (high vac.), $[\alpha]_D$ +4·6°. Gradual addition of Br–$CHCl_3$ to (**IX**) in boiling $CHCl_3$ leads to a *compound*, $C_{33}H_{49}O_8Br$, m.p. 215—225° (decomp.), $[\alpha]_D$ +38·6°, and an isomeric *Br-ketone*, m.p. 293—294·5°, $[\alpha]_D$ +81°; both substances give a yellow colour with $C(NO_2)_4$. Prolonged contact of (**IX**) with 33% HBr–AcOH at room temp. gives (**X**), hydrolysed by alkali to the 2 : 13-(*OH*)$_2$-derivative, m.p. >370°. (**X**) is oxidised by SeO_2 in dioxan at 200—210° to an acidic substance and the 13 : 28-*lactone* of enol-7 : 8-diketo-13-hydroxy-2-acetoxyoleanane-28-carboxylic acid, m.p. 265—267°, $[\alpha]_D$ −30°, which could not be acetylated by Ac_2O in C_5H_5N or by Ac_2O and the BF_3–Et_2O complex, and is hydrolysed by boiling 5% KOH–MeOH to the corresponding 2-*OH*-derivative, m.p. 325—327°, into which it is re-converted by Cu_2O–BF_3–Et_2O. Slow oxidation of (**IV**) by CrO_3 and H_2SO_4 in AcOH at room temp. affords *Me* $\Delta^{12:13}$-2 : x-*diketo-oleanene*-28-*dicarboxylate*, m.p. 190—191° after loss of MeOH of crystallisation at 110—114°, $[\alpha]_D$ +35·2° [*oxime*, m.p. 265—267° (decomp.); *semicarbazone*, m.p. 257—258° (decomp.)], which gives a marked yellow colour with $C(NO_2)_4$. The non-cryst. *Me* $\Delta^{12:13}$-2-keto-*x*-acetoxyoleanene-28-carboxylate, obtained analogously from the 2-OH-compound, gives an *oxime*, m.p. 151—152° (decomp.), and a *semicarbazone*, m.p. 216—218° (decomp.). (**VI**) is oxidised by SeO_2 in boiling AcOH to *Me* $\Delta^{12:13-18:19}$-2 : x-*diacetoxyoleadiene*-28-*carboxylate*, m.p. 234—235° $[\alpha]_D$ −156·0°, which gives a brown colour with $C(NO_2)_4$; in dioxan at 200° the product is *Me* $\Delta^{10:11-13:18}$-12 : 19-*diketo*-2 : x-*diacetoxyoleadiene*-28-*carboxylate* (**XI**), m.p. 230—231°, $[\alpha]_D$ −189° (a second *modification*, m.p. 211°, is sometimes obtained), which does not give a yellow colour with $C(NO_2)_4$ and is hydrolysed by very prolonged boiling with 10% KOH–MeOH to $\Delta^{10:11-17:18}$-12 : 19-*diketo*-2 : x-*dihydroxy*-28-*noroleadiene* (**XII**), m.p. 300—302°, $[\alpha]_D$ +228° (2-*acetate*, m.p. 264°, $[\alpha]_D$ +212°), and $\Delta^{10:11-13:18}$-12 : 19-diketo-2 : x-dihydroxyoleadiene-28-carboxylic acid, which passes in boiling xylene into (**XII**). (**XI**) is transformed by boiling 5% HCl–MeOH into *Me* $\Delta^{10:11-13:18}$-12:19-*diketo*-2-*hydroxy*-x-*acetoxyoleadiene*-28-*carboxylate*, m.p. 310—312°, which does not give a yellow colour with $C(NO_2)_4$. With N_2H_4,H_2O in EtOH at 200° (**XII**) gives a *pyridazine* derivative, $C_{29}H_{40}O_2N_2$, decomp. ~350°, $[\alpha]_D$ +283°. M.p. are corr. $[\alpha]_D$ are in $CHCl_3$. H. W.



Triterpene resinols and related acids. XV. Dehydration of α-amyrin and α-amyradienol with phosphoric oxide : *l*-α-amyradiene and *l*-α-amyratriene. E. S. Ewen, A. E. Gillam, and F. S. Spring (*J.C.S.*, 1944, 28—30).—Dehydration of α-amyrenonol with AcOH–HI gives *α-amyradienone*-III, m.p. 179°, $[\alpha]_D^{20}$ +170°. α-Amyradienol (**I**) with PCl_5 yields *α-dichloroamyradiene*, m.p. 128—129°, $[\alpha]_D$ +407°, which with AcOH–Zn affords d-*α-amyratriene*, m.p. 131—133°, $[\alpha]_D$ +439°. Dehydration of (**I**) with P_2O_5 leads to l-*α-amyratriene*, m.p. 140—142°, $[\alpha]_D^{20}$ −450°, which contains a conjugated triene system (absorption spectrum). The ethenoid linking of α-amyrin must consequently be situated in the vicinity of the OH. All rotations are in $CHCl_3$. F. R. S.

Chemical composition of *Calotropis gigantea*. I. Wax and resin components of the latex. P. B. R. Murti and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1943, **18, A**, 145—159).—The latex of *C. gigantea* is converted by EtOH into a soft coagulum (*A*) and an aq. alcoholic solution (*B*). (*A*) is transformed by successive extractions with boiling EtOH and Et_2O into a sticky solid which has not been investigated completely, a small amount of a substance, m.p. 248—250°, and a residue which is hydrolysed to AcOH and $Pr^{\beta}CO_2H$ and mixtures of resinols which are separated into their components by acetylation or benzoylation followed by fractional crystallisation. Thus are obtained : α-*calotropeol* (**I**), $C_{30}H_{50}O$, m.p. 204—205°, $[\alpha]_D$ +102·0° in C_6H_6 (*acetate*, m.p. 250—251°, +98·0° in C_6H_6; *benzoate*, m.p. 273—274°, $[\alpha]_D$ +743° in C_6H_6), which gives a bright pink solution immediately with the Liebermann–Burchard reagent, an orange-yellow solution with deep green fluorescence with Salkowski's reagent, and appears to contain one double linking; β-*calotropeol*, $C_{30}H_{50}O$, m.p. 216—217° (*benzoate*, m.p. 279—280°, $[\alpha]_D$ +69·0° in C_6H_6; *acetate*, m.p. 238°, $[\alpha]_D^{30}$ +43·9°), which resembles (**I**) in its colour reactions; a mixture of β-amyrin and tetracyclic resinols. (*B*) yields to Et_2O–$CHCl_3$ a cryst. substance (? mixture), m.p. ~242°, indicated by its colour reactions and solubility to belong to the cardiac poisons and containing N and S; CaC_2O_4 is also present in very fine subdivision. H. W.

VI.—HETEROCYCLIC.

Additive compounds of organo-magnesium derivatives with furanoid compounds. E. Cherbuliez and M. K. Araqui (*Helv. Chim. Acta*, 1943, **26**, 2251—2252).—Coumarone, coumaran, diphenylene oxide (**I**), or methylcodeine (**II**) in C_6H_6 is added to MgMeI, MgEtBr, MgPhBr, or $CH_2Ph{\cdot}MgCl$ in Et_2O. The Et_2O is distilled off and the residual solution is boiled for 0·5—2 hr., whereby the additive *compound* is gradually pptd., usually almost quantitatively. Substitution of C_6H_6 by PhMe does not alter the change. Substances closely allied to (**II**) such as thebaine and deoxycodeine react with organo-magnesium compounds in Et_2O with rupture of the furanoid ring. (**I**) is obtained in 28% yield by heating PhOH with PbO at 170° until H_2O ceases to be evolved and then distilling the product rapidly with a free flame. H. W.

Transformation products of simpler benzopyrylium compounds. P. Karrer, C. Trugenberger, and G. Hamdi (*Helv. Chim. Acta*, 1943, **26**, 2116—2120; cf. A., 1943, II, 101; Pratt *et al.*, *J.C.S.* 1923, **123**, 745).—3 : 4′-Dimethoxy-2-phenylbenzopyrylium ferrichloride (**I**), m.p. 150—151° (lit. 135°), is obtained directly by passing HCl into a solution of *o*-OH·C_6H_4·CHO (**II**) and *p*-OMe·C_6H_4·CO·CH_2·OMe (**III**) in abs. EtOH; the corresponding *chloride* (**IV**), m.p. 109°, is almost quantitatively obtained by passing HCl into (**II**) and (**III**) in AcOH. (**I**) is transformed by hot MeOH containing NaOAc into the *Me ether* (**V**) of the carbinol base, m.p. 149°, more readily prepared from (**IV**) and cold MeOH; the corresponding *Et ether* has m.p. 132°. (**V**) and BzO_2H in $CHCl_3$ give 2 : 3 : 4′-*trimethoxyflavanone*, m.p. 220°, hydrolysed (HCl in boiling aq. MeOH) to 4′-methoxyflavanol, m.p. 230° (lit. 225°). (**V**) and Br in $CHCl_3$ afford 3 : 4′-*dimethoxy*-2-*phenylbenzopyrylium perbromide*, m.p. 143°, reconverted into (**V**) by MeOH. COPh·CH_2·OMe and (**II**) in anhyd. HCO_2H saturated with dry HCl at room temp. give 3-*methoxy*-2-*phenylbenzopyrylium chloride*, m.p. 119° (corresponding *perbromide*, m.p. 122°), converted by H_2O into the corresponding carbinol *base*, m.p. 121°, which in hot EtOH smoothly gives the *Et ether*, m.p. 124°. H. W.

Reaction between quinones and metallic enolates. Mechanisms.—See A., 1944, II, 103.

1 : 3-Dioxans.—See B., 1944, II, 35.

***lin.*-Dibenzothionaphthen in coal tar.** O. Kruber and L. Rappen (*Ber.*, 1940, **73**, [*B*], 1184—1186).—The solid residue obtained from the C_5H_5N mother-liquors used in the purification of chrysene from coal tar are extracted with EtOH containing 10% of xylene. The undissolved material is oxidised by 30% H_2O_2 in AcOH at 100° to dibenzothionaphthen sulphone (**I**), m.p. 231°, thus establishing the presence of *lin.*-dibenzothionaphthen (**II**) in coal tar. Successive addition of S and $AlCl_3$ to 2-$C_{10}H_7$Ph at 110° and subsequent heating of the mixture to 200° give a product from which (**I**) can be obtained by oxidation but from which (**II**) could not be isolated. Brasan is transformed by molten KOH at 280—320° into 3-*hydroxy*-2-*o-hydroxyphenylnaphthalene*, converted into (**II**), m.p. 160° (picrate, m.p. 128°), by distillation with P_2S_5 in a vac. The distillate contains also a substance which is oxidised (H_2O_2 in AcOH) to a *sulphone*, m.p. 264°. H. W.

Piperidine derivatives.—See B., 1944, II, 35.

Iron derivatives of heterocyclic acids. I. Ferric complexes of chelidamic acid. J. H. Gorvin (*J.C.S.*, 1944, 25—28).—Picolinic acid and $Fe(OH)_3$ give *tripicolinato-iron* ($+H_2O$), decomp. 282° (corr.), and *di-(4-chloropicolinato)hydroxo-iron*, darkens 260—270°, is obtained from the Cl-acid. Chelidamic acid with $Fe(OH)_3$ forms *dichelidamatoferric acid* ($+2H_2O$) (**I**), which affords NH_4 ($+2{\cdot}5H_2O$), NEt_4 ($+2H_2O$), o-*toluidine*, C_5H_5N, *quinoline*, *quinine*, *Na* ($+2H_2O$), *K* ($+2H_2O$), *Ag* ($+2H_2O$), *Ba* ($+2{\cdot}5H_2O$), *di*-p-*toluidine* ($+H_2O$), decomp. 220—225°, and *dinor*-d-*ψ-ephedrine* salts; Ag_3 and *triaquoferric dichelidamato-oxoferrate* ($+4H_2O$). (**I**) contains one free and one masked CO_2H, and gives rise to two series of H_2O-sol. salts. The light-absorption of the complexes has been studied. F. R. S.

Azo-dyes. I. Preparation and bacteriostatic properties of azo-derivatives of 2 : 6-diaminopyridine. R. N. Shreve, M. W. Swaney, and E. H. Riechers (*J. Amer. Chem. Soc.*, 1943, **65**, 2241—2243).—2 : 6-*Diamino-3-arylazopyridine monohydrochlorides* are prepared in which aryl = Ph (**I**), m.p. 137°, *o*-, m.p. 184°, *m*-, m.p. 123·2°, and *p*-tolyl, m.p. 151·3°, *o*-, m.p. 193°, *m*-, m.p. 99·5°, and *p*-anisyl, m.p. 192°, *o*-, m.p. 127°, and *m*-$OEt{\cdot}C_6H_4$, m.p. 114·3°, *o*-, m.p. 189°, *m*-, m.p. 209·4°, and *p*-$OH{\cdot}C_6H_4$, m.p. 232°, *m*-C_6H_4Cl, m.p. 259°, *o*-, m.p. 209·5°, *m*-, m.p. 141°, and *p*-C_6H_4I, m.p. 198°, 5 : 1 : 2-, m.p. 222°, and 6 : 1 : 3-$OH{\cdot}C_6H_3Me$, m.p. 203—204°, 3 : 1 : 4-, m.p. 233°, 4 : 1 : 2-, m.p. 265°, and 5 : 1 : 2-$NO_2{\cdot}C_6H_3Me$, m.p. 251°, 2 : 5 : 1-$OMe{\cdot}C_6H_3Cl$, m.p. 204°, 5 : 2 : 1-$NO_2{\cdot}C_6H_3(OMe)$, m.p. 226°, 4 : 1 : 3-$OMe{\cdot}C_6H_3Me$, m.p. 174·5°, 1 : 3 : 2-$C_6H_3Me_2$, m.p. 122°, *o*-, m.p. 135·6°, and *p*-C_6H_4Ph, m.p. 230·5°, *p*-$PhN_2{\cdot}C_6H_4$, m.p. 203—204°, *o*-$CO_2Me{\cdot}C_6H_4$, m.p. 177°, and *o*-$CO_2Et{\cdot}C_6H_4$, m.p. 170°. M.p. are corr. Solubilities in H_2O are recorded, that of (**I**) being much the highest. For bacteriostatic properties, see A., 1944, III, 295. R. S. C.

Invert soaps. V. Quaternary salts of isomeric hydroxyquinoline ethers. R. Kuhn and O. Westphal (*Ber.*, 1940, **73**, [*B*], 1105—1108; cf. A., 1944, II, 98).—3-Amino- is obtained (92%) from 3-bromo-quinoline by conc., aq. NH_3 and CuO at 140—150°. The K salt (pptd. by KOEt–EtOH) of 3-hydroxyquinoline with *n*-$C_{12}H_{25}Br$ in EtOH at 180° gives 3-n-*dodecyloxyquinoline*, m.p. 42° [*methylmethosulphate* (**I**), m.p. 115—116°]. 8-n-*Dodecyloxyquinoline*, m.p. 25°, b.p. 225°/3 mm. [*hydrochloride*, m.p. 73—80°; *methylmethosulphate* (**II**), m.p. ~23°], is similarly prepared. *n*-$C_{12}H_{25}Cl$ gives 6-n-*dodecyloxyquinoline*, m.p. 45°, b.p. 235°/2 mm. [*hydrochloride*, m.p. 150—151°; *methylmethosulphate* (**III**), m.p. 70° (decomp.)]. Bactericidal and bacteriostatic activities of (**I**), (**II**), (**III**), and *n*-$C_{12}H_{25}{\cdot}NMe_2Br{\cdot}CH_2Ph$ are very similar. R. S. C.

Polarisation of fluorescence and anisotropy of molecules of dyes.—See A., 1944, I, 77.

***cyclo*Tetramethylenepyrazolone. III. Molecular compounds.** H. Ruhkopf (*Ber.*, 1940, **73**, [*B*], 1066—1068; cf. A., 1940, II, 108).—By mixed m.p. diagrams [only eutectics and m.p. of compounds (in parentheses below) are recorded] it is shown that 1-phenyl-2-methyl-3 : 4-*cyclo*tetramethylene-5-pyrazolone form 1 : 1 additive *compounds* with $CHPhEt{\cdot}CO{\cdot}NH_2$ (m.p. 92°), $CHPhPr^{\alpha}{\cdot}CO{\cdot}NH_2$ (m.p. 78°), $CHPh_2{\cdot}CO{\cdot}NH_2$ (m.p. 125°), and phenylethylhydantoin (m.p. 146°), and a 1 : 2 additive *compound*, m.p. 128°, with α-allyl-Δ^{γ}-pentenoylcarbamide, but no compound with $CHR_2{\cdot}CO{\cdot}NH_2$ (R = Et, Pr^{α}, or allyl), α-*cyclo*hexenyl-*n*-propionamide, $CH_2Ph{\cdot}CO{\cdot}NH_2$, $CHRR'{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2$ (R = R' = Et or Pr; R = Ph, R' = Et), or diketopyrazolidine. It is similarly shown that no compounds are formed from (*a*) 1-phenyl-2-methyl-3 : 4-*cyclo*trimethylene-5-pyrazolone with $CHPhEt{\cdot}CO{\cdot}NH_2$, $CHPh_2{\cdot}CO{\cdot}NH_2$, or $CHR_2{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2$ (R = Et, Pr, or allyl), (*b*) 1-phenyl-2 : 3-dimethyl-5-pyrazolone with $CHPhEt{\cdot}CO{\cdot}NH_2$ or phenacetin, or (*c*) 4-dimethylamino-1-phenyl-2 : 3-dimethyl-5-pyrazolone (**I**) with $CHR_2{\cdot}CO{\cdot}NH_2$ (R = Et or Ph), $CHPhEt{\cdot}CO{\cdot}NH_2$, or phenacetin, but that (**I**) gives a 1 : 1 additive *compound*, m.p. 147°, with phenylethylhydantoin. From these results general rules are propounded. R. S. C.

Pyrimidines.—See B., 1944, III, 34.

Synthesis of carbazo-condensed systems from α- and α'-aminonicotines. V. Synthesis of 3-phenylpyriminazole and its nicotine analogue. J. L. Goldfarb and M. S. Kondakova (*J. Appl. Chem. Russ.*, 1942, **15**, 151—163; cf. 1937, A., II, 473).—2-Aminopyridine (**I**) and $CHPhBr{\cdot}CO{\cdot}CO_2H$ in aq. $NaHCO_3$ yield, besides $COPh{\cdot}CH_2{\cdot}OH$ and $CH_2Ph{\cdot}CO_2H$, 3-phenylpyriminazole-2-carboxylic acid, m.p. 201—202° (decomp.) (*hydrochloride*, m.p. 225—227°; *hydrobromide*, m.p. 246°; *platinichloride*, m.p. 243—247°; *picrate*, m.p. 205—207°), which at 210—220° gives 3-*phenylpyriminazole*, m.p. 97—98°, b.p. 188—192°/6 mm. (*hydrobromide*, m.p. 195°; *platinichloride* does not melt up to 285°; *picrate*, m.p. 236°), giving with aq. $KMnO_4$ (**I**) and with Br–H_2O a Br additive product. 2-Aminonicotine (**II**) and $CHPhBr{\cdot}CO{\cdot}CO_2H$ in aq. $NaHCO_3$ give 7-(*N*-methylpyrrolidyl)-3-phenylpyriminazole-2-carboxylic acid, which could not be isolated but gave a *picrate*, m.p. 210—211° (decomp.), and at 230—240° afforded 7-(*N-methylpyrrolidyl*)-3-*phenylpyriminazole*, m.p. 94—95° [*picrate*, m.p. 240° (decomp.)], which is oxidised by CrO_3 to (**II**). J. J. B.

Pyridylquinolines.—See B., 1944, II, 66.

Invert soaps. VI. Triazolium salts. R. Kuhn and O. Westphal (*Ber.*, 1940, **73**, [*B*], 1109—1113; cf. A., 1934, II, 111).—The K salt of 1 : 2 : 4-triazole and *n*-$C_{12}H_{25}Cl$ in EtOH at 110° gives 1-n-*dodecyl*-1 : 2 : 4-*triazole*, m.p. 39° [*ethobromide*, m.p. 150—152°]. The K or Na salt of benztriazole with AlkCl in EtOH at 100—120° gives 60—80% of 1-alkylbenztriazole but AlkBr affords 1 : 3-dialkylbenztriazolium bromide. Thus are obtained 1-n-*dodecyl*-, m.p. 44—46° [3-*methylmethosulphate*, m.p. ~25°; 3-*ethobromide* (**I**), m.p. 27°; *butylobromide*, m.p. 33°], and 1-n-*hexadecyl*-*benztriazole*, m.p. 62° (3-*methylmethosulphate*, m.p. 76—77°; 3-*ethobromide*, m.p. 96—97°), 1 : 3-*dioctyl*-, m.p. 147—148°, and 1 : 3-*di*-n-*dodecyl*-*benztriazolium bromide*, m.p. 141—143°, and 1 : 3-*dibenzylbenztriazolium chloride*, m.p. 207—209°. Bactericidal and bacteriostatic activities of the salts against six bacteria are recorded. The activity of (**I**) is of exceptional degree. R. S. C.

Fluorescence of chlorophyll.—See A., 1944, I, 77.

Constitution of yeast-ribonucleic acid. VII. Diffusion coefficients and mol. wts. W. E. Fletcher, J. M. Gulland, D. O. Jordan, and (in part) H. E. Dibben. **VIII. Electrometric titration of the acid groups.** W. E. Fletcher, J. M. Gulland, and D. O. Jordan (*J.C.S.*, 1944, 30—33, 33—39; cf. A., 1944, II, 85).—VII. Diffusion coeffs. suggest that yeast-ribonucleic acids (**I**) of different origins have mol. wts. ranging between those corresponding with 8 and 18 hypothetical tetranucleotides. Deamination of B.D.H. (**I**) under the special conditions described does not diminish the mol. wt., confirming the conclusion that phospho-amide groups are not essential links between nucleotides in that acid. Less controlled conditions cause extensive mol. degradation.

VIII. Electrometric titration of samples of (**I**) indicates that (**I**) has four acid dissociations per tetranucleotide when existing as a polytetranucleotide, three of which are primary dissociations, and one a secondary dissociation of H_3PO_4. The deaminated acid is similarly constituted. Mild hydrolysis reduces the mol. wt. of the polytetranucleotide, and the titration results suggest that a further secondary dissociation of H_3PO_4 becomes free. These data necessitate a modification of the formula previously proposed for (**I**); this is discussed in relation to the existing mol. wt. and enzyme data. F. R. S.

Nucleic acids. XVI. Constitution of thymonucleic acid. Position of the linking between bases and deoxyribose. H. Bredereck, G. Müller, and (Miss) E. Berger. **XVII. Nucleotide syntheses. Synthesis of uridylic acid.** H. Bredereck, and (Miss) E. Berger (*Ber.*, 1940, **73**, [*B*], 1058—1065, 1124—1125).—XVI. Linkage of the sugar to positions 9 and 3 is proved for purine and pyrimidine deoxyribonucleotides, respectively (cf. Gulland *et al.*, A., 1938, II, 128, 296). Adding Me_2SO_4 and aq. NaOH to Na thymonucleate at 30—35° and pH 8—9 gives a Na salt (**I**) containing 7 NMe and 2 OMe; further methylation slightly increases the OMe but not the NMe content. Fission of (**I**) by emulsin at 37° and pH 4·9 causes an increase of 4 equivs. in acidity so that the methylated acid is tetrabasic; one Me is probably present as phosphoric ester. Passing gaseous HCl into (**I**) in 95% MeOH gives 1 : $N_{(6)}$-dimethyladenine, $CH{<}\begin{matrix}N{=}C{\cdot}C(.NMe){\cdot}NMe\\ NH{\cdot}C\text{———}N{\cdot}CH\end{matrix}$ (*picrate* m.p. 235°), also obtained (picrate, m.p. 236°) from adenosine by Me_2SO_4–NaOH and then HCl–MeOH. With 25% H_2SO_4 at 175—180° (**I**) gives 1 : $N_{(6)}$-dimethylcytosine, $\begin{matrix}NH{\cdot}CO{\cdot}NMe\\ CH{:}CH{\cdot}C{:}NMe\end{matrix}$ (*picrate*, m.p. 222°) [also obtained (picrate, m.p. 218°) from cytidine nitrate by Me_2SO_4–NaOH and then 25% H_2SO_4 at 175—180°], and (? 1-)methylthymine, m.p. 210° (A., 1908, i, 835, m.p. 202—205°), but no methylguanine. Me_2SO_4–NaOH and then HCl–MeOH converts guanosine into a dimethylguanine (*hydrochloride*, m.p. 275°; *picrate*, m.p. 214°).

XVII. Triphenylmethyluridine (A., 1933, 149) with $(OPh)_2POCl$ in C_5H_5N at −18° and then aq. NaOH at 100° gives uridylic acid, isolated as brucine salt, sinters 188°, m.p. 195°, $[\alpha]_D^9$ −54·8°. Known processes yield 3 : 5-*benzylideneguanosine*, m.p. 295° (2-*acetate*, m.p. 263°), *guanosine* 2-*acetate*, m.p. ~180°, and *guanosine* 5-*CPh*$_3$ *ether*, amorphous (2-*acetate*, amorphous). R. S. C.

Aminothiazoles and benzenesulphommidothiazolines etc.—See B., 1944, II, 34, 35.

Ring fissions with thiazolium salts. A. Schöberl and M. Stock (*Ber.*, 1940, **73**, [*B*], 1240—1252).—Addition of CH_2PhBr to 2 : 4-dimethylthiazole gives 3-benzyl-2 : 4-dimethylthiazolium bromide (**I**), m.p. 171°. Interaction of $COMe{\cdot}CH_2Cl$ with $MeCS{\cdot}NHPh$ at 15—20° gives S-*acetonylthioacetanilide hydrochloride*, which passes when heated or boiled with alkali and subsequently acidified into 3-phenyl-2 : 4-dimethylthiazolium chloride, transformed by KI into the corresponding iodide (**II**), which gives an intense blue colour with phosphotungstic acid and a red colour with Na nitroprusside after addition of NH_3. The initially yellow solution of (**I**) in 2N-

NaOH becomes colourless when heated but addition of acid does not cause liberation of H_2S and there is no production of PbS on boiling with alkali plumbite; the parallel experiment with aneurin is positive. In alkaline solution (I) is immediately oxidised by I and is converted by air into a substance, m.p. (indef.) 96—97°. Gradual addition of AcOH to a solution of (I) or (II) in 2N-NaOH–EtOH containing $NaNO_2$ causes the development of an intense yellow colour which does not appear to be very sensitive. When 9(18)-phosphotungstic acid is added to solution of (I), (II), or aneurin (III) which has been kept for some time an intense blue colour appears which can be used in the detection and determination of thiazolium salts. Addition of freshly prepared Na nitroprusside solution to aq. solutions of (I) and (II) which have been treated with 2N-NH_3 causes the appearance of a cherry-red colour which attains its max. after a time and is very stable. The colour does not appear in 2N-NaOH and is markedly less stable in 0·1N-NaOH than in NH_3. It is not given by (III). The test can be used quantitatively. Increase of temp. (55—60°) facilitates the development of the colour, which does not then reach its full intensity since decomp. is also facilitated. The solutions are rapidly bleached by exposure to light. They are, however, stable for days in the dark. They should be prepared in a subdued red light and exposed as briefly as possible to the photometer light. NH:CMe·SH and OH·CH:CCl·CO_2Et are condensed and then hydrolysed to *2-methylthiazole-5-carboxylic acid*, m.p. 209° (decomp.) (*Et* ester, b.p. 117—120°/19 mm.), not identical with the acid thus described in the literature. 2-Methylthiazole-4 : 5-dicarboxylic acid, m.p. 169°, loses CO_2 at 175° with production of a monocarboxylic acid, m.p. 143—145°, softens at 130°. H. W.

Reactions of benzthiazole derivatives. IV. 1-Thiocyanobenzthiazole. W. H. Davies and W. A. Sexton (*J.C.S.*, 1944, 11—13).—1-Thiocyanobenzthiazole (I) is not stable to prolonged storage and decomposes fairly rapidly when heated. With many reagents, *e.g.*, NaOH and Na_2S, it is converted into derivatives of 1-thiolbenzthiazole. With MeOH, (I) gives mainly *Me benzthiazyl-1-thioncarbamate*, m.p. 175° (*Et* compound, m.p. 163°, from EtOH). The mechanism of this reaction is discussed. F. R. S.

Cyanine type dyes.—See B., 1944, II, 58, 90, 91.

Dioxazine dyes.—See B., 1944, II, 69.

VII.—ALKALOIDS.

Fluorescent alkaloid in rye-grass (*Lolium perenne*, L.). I. Introduction. R. E. R. Grimmett and J. Melville. **II. Extraction from fresh rye-grass and separation from other bases.** R. E. R. Grimmett and D. F. Waters. **III. Extraction and properties.** I. Reifer and N. O. Bathurst. **VI. Investigation of a volatile base C_6H_7N.** F. B. Shorland, E. P. White, and R. E. R. Grimmett (*New Zealand J. Sci. Tech.*, 1943, **24**, B, 149—150, 151—155, 155—159, 179—185; cf. A., 1944, III, 282; also C, 1944, Part 2).—I. A neutral or acid EtOH extract of the basal shoots of rye-grass, from which anthocyanins and fat-sol. pigments have been removed, gives an intense greenish fluorescence on addition of NH_3. This is due to an alkaloid, named *perloline* (I). Other alkaloids are present in smaller amount.

II. The only other pasture species to give comparable yields of (I) is tall fescue. For bulk extraction, grass of >0·02% alkaloid content is chosen by spot testing. 60—70% of (I) in the grass is extracted by 0·75% HCl. Neutralisation with $Ca(OH)_2$ and adjustment of pH to 7·5 with Na_2CO_3 gives a sludge containing 50—60% of (I) in the extract; if tannic acid is also added, 90% is pptd.; approx. quant. extraction of the sludge is effected by excess of Na_2CO_3 and EtOH. (I) is finally separated from other bases by its greater basicity, and its hydrochloride is crystallised out of a solution conc. below 50°. Fraction "B" contains other $CHCl_3$-sol., Et_2O-insol. bases, similar to (I), but less fluorescent. Fraction "C" contains an Et_2O-sol. *base*, subliming at 295° (180°/0·04 mm.), decomp. 316°; the *hydrochloride* (subliming at 297°, decomp. 317°) gives a bright blue fluorescence in aq. solution, and characteristic ppts. with KI_3, $KBiI_4$, $KHgI_3$, $AuBr_3$, and $HgCl_2$. Fraction "D" (II) was sol. in ligroin and had an odour like C_5H_5N.

III. Dried ground rye-grass leaves are extracted with EtOH and AcOH. Dried unground grass is extracted with 1% H_2SO_4. Purification of (I) is carried out by partition between $CHCl_3$ and dil. HCl; after 7 crystallisations from H_2O, the hydrochloride analyses for $C_{36}H_{22}O_3N_4(OMe)_4,2HCl$. 0·2 p.p.m. can be detected in daylight by the fine green fluorescence of solutions in $CHCl_3$ or EtOH, which are not stable to direct sunlight. Ppts. are given with $AgNO_3$, picric acid, $HgCl_2$, $KBiI_4$, $KHgI_3$, phospho-molybdic and -tungstic acids, $AuCl_3$, $PtCl_4$, KI_3, and NH_4 reineckate, and colours with $NaVO_3$–H_2SO_4 (brown) and Ti_2O_3–H_2SO_4 (brick-red). Oxidation ($KMnO_4$ or H_2O_2) gives a colourless base with blue fluorescence, and reduction ($TiCl_3$) a non-fluorescent material. The alkaloid content of rye-grass varies with environmental conditions from traces to 0·1%.

VI. (II) is almost entirely a *base*, C_6H_7N, b.p. 134—138° (*picrate*, m.p. 154—156°, *mercurichloride*, m.p. 151—152°), which can be reduced catalytically to a H_6-derivative (*hydrochloride* m.p. 169—171°; 3 : 5-*dinitrobenzoate*, m.p. 110—112°). (II) is not a picoline; possible formulæ are discussed. S. A. M.

VIII.—ORGANO-METALLIC COMPOUNDS.

Mode of reaction of lithium phenyl. V. Behaviour of halogenated anisoles towards lithium phenyl. G. Wittig and G. Fuhrmann (*Ber.*, 1940, **73**, [*B*], 1197—1218).—The halogenated anisoles are allowed to react with LiPh in Et_2O under comparable conditions and investigation is made of the products formed after addition of H_2O or $COPh_2$. In the reaction of the *o*-halogenoanisoles it is found that I is replaced rapidly and Br more slowly by Li whereas Cl and F (the latter more rapidly than the former) give the Li halide with consequent formation of *o*-C_6H_4Ph·OMe. H between OMe and halogen in the *meta*-compounds is readily exchanged for Li and in consequence of this action the formation of C_6H_4Ph·OMe and LiHal predominates. In comparison the exchange of halogen for metal, which is observed only with *m*-C_6H_4I·OMe, recedes into the background. Common to *para*-substituted anisoles is the replacement of "mobile" H by metal which is facilitated by increasingly electronegative character of the halogen and with *p*-C_6H_4F·OMe results in the production of *p*-C_6H_4Ph·OMe. *p*-C_6H_4I·OMe and *p*-C_6H_4Br·OMe also exchange their halogen for Li. The exchangeability of aromatically bound H for Li depends on the polarisation of C-H linkings by electronegative substituents such as OMe or F and is explicable by the theory of induced alternating polarities. Since the acidifying effect diminishes with increasing distance only H in the *ortho*-position is replaceable and the entry of Li to the C_6H_6 nucleus is facilitated by the presence of 2 *meta*-substituents between which the Li enters. The influence of OMe and the 4 halogens on the action is qualitatively but not quantitatively similar to the effect on the acidity of AcOH. The theory fails to explain the observation that the exchange of H for Li is considerably facilitated by an accumulation of negative substituents even in the *para*-position. Here the alternating induction is subsidiary to a second effect which behaves as a "general effect" from C to C and, for example, causes the acidifying effect of a halogen in a fatty acid to diminish with increasing distance from CO_2H. Steric effects are also obvious. If Li replaces H *ortho* to halogen as has been established for PhF and is observed with *m*-halogenoanisoles, the halogen becomes so reactive and the subsequent production of Ph_3 derivatives under the further influence of LiPh is so rapid that in only one case it has been possible to trap the metallic compound as the carbinol by use of $COPh_2$. A polarising counter action of Li corresponds with the polarising action of halogen. An electronic explanation of the replaceability of halogen by Li is advanced. The following appear new: 1 : 6(or 1 : 8)-*dimethoxy*-9 : 9-*diphenylfluorene*, m.p. 201—202°; 1-*methoxy*-, dimorphic, m.p. 180·5—181° and 193—194°, converted by Br in boiling AcOH into 2(or 4)-*bromo*-1-*methoxy*-9 : 9-*diphenylfluorene*, m.p. 222·5—223°; 5-*iodo*-, m.p. 136—137°, 5-*chloro*-, m.p. 118—119°, and 5-*fluoro*-3-*methoxytriphenylcarbinol*, m.p. 129·5—131°. *m*-C_6H_4Ph·OMe is converted by successive treatments with LiPh in Et_2O and $COPh_2$ into 2-*methoxy*-4-*phenyltriphenylcarbinol*, m.p. 138·5—139·5°. Under similar treatment veratrole gives 2 : 3-*dimethoxytriphenylcarbinol*, m.p. 110—111·5°. 1 : 2 : 3-$C_6H_3(OMe)_3$ is converted by LiPh in Et_2O followed by $COPh_2$ and then by 2N-NaOH into 1 : 3 : 2-$(OMe)_2C_6H_3$·ONa (whence the benzoate, m.p. 114—116°); other products are unchanged material, CPh_3·OH, and 2 : 3 : 4-trimethoxytriphenylcarbinol, m.p. 140—140·8° (lit. 139°). 1 : 3 : 5-$C_6H_3(OMe)_3$ when treated similarly yields 2 : 4 : 6-trimethoxytriphenylcarbinol, m.p. 114—115° (lit. 110—111°). H. W.

Mercury diallyl. K. V. Vijayaraghavan (*J. Indian Chem. Soc.*, 1943, **20**, 318; cf. A., 1942, II, 41).—CH_2:CH·CH_2·HgI (I) and conc. aq. KCN give $(CH_2$:CH·$CH_2)_2$Hg (II). Fresh aq. suspensions of (I) give a faint odour of (II) with $Na_2S_2O_3$, Na_2S, or KI on keeping or gently warming; on heating Hg and complex inorg. Hg salts are formed. (I) in EtOH with Na_2S or $Na_2S_2O_3$ ppts. Hg and gives inorg. complex salts; with KI–EtOH it gives a faint odour of (II) on warming, but K_2HgI_4 on heating. (I) in COMe$_2$ with NaI gives a faint odour of (II), but is mainly unchanged. S. A. M.

IX.—PROTEINS.

Denaturation changes in ovalbumin with urea, radiation, and heat. J. H. Clark (*J. Gen. Physiol.*, 1943, **27**, 101—111).—When 10—50% of $CO(NH_2)_2$ (I) is added to isoelectric solutions of ovalbumin (II) the pH val. is altered to ~5·2—5·8 depending on the concn. of (I). The extent of the denaturation produced by (I) depends on concns. of (I) and (II) and also on the temp. of the solution. 0·9% (II) solution is not denatured by 20% (I); it is denatured slowly by 25% and rapidly by 35% (I) at room temp. At higher temp. 30% (I) is rapidly effective. Denaturation of (II) by ultra-violet radiation or heat is accompanied by structural changes but the mol. has a fair degree of symmetry except at the isoelectric point, and

there is no association or dissociation of the mol. within the pH range outside the zone in which aggregation follows denaturation. Denaturation of (II) by (I) causes no change in optical rotation until the concn. of (I) is high enough to dissociate the mol. The optical rotation of fresh native (II) does not vary over the pH range 3·4—10·5, but it is increased ~100% after boiling the solution for 5 min. at pH 3·4 or 6·4—7·2, and the increase is the greater the nearer is the pH to the isoelectric point. In presence of (I) a (I)–protein complex is formed in which the protein is denatured but is not pptd. because of the dispersive action of (I); this prevents pptn. of protein exposed to ultra-violet radiation and subsequent heating to 40° because the complex is not decomposed at 40°. Decomp. occurs at 55—58° so that aggregation results at a temp. < that of rapid heat-denaturation. This is not due to an acceleration of heat-denaturation or to decrease in the temp. of heat-denaturation but results from the effect of heat on the complex which liberates the (I)-denatured protein and causes its pptn. J. N. A.

Invert soaps. I. Action of invert soaps on albuminous substances. R. Kuhn and H. J. Bielig [in part, with O. Dann] (*Ber.*, 1940, **73**, [*B*], 1080—1091).—Invert soaps ppt. the echinochrome symplex from H_2O or aq. Na_2CO_3, the ppt. retaining the dye tenaciously (cf. Kuhn *et al.*, A., 1943, III, 738). In dil. AcOH invert soaps liberate the dye (removed by Et_2O) with pptn., and subsequent addition of Na_2CO_3 ppts. the almost colourless protein. A 1% solution of invert soap gives with chloroplastin a ppt. containing all the chlorophylls and carotenoids in extractable (Et_2O, C_6H_6) form; as the concn. of n-$C_{12}H_{25}$·SMe_2I (I) added is increased, the amount of dye liberated slowly increases; this amount suddenly becomes much greater, approx. when the drop no. of the soap solution is a max. (0·2% solution); an approx. parallelism also exists between the amount of dye liberated and the surface activity of various sulphonium iodides. ~30 mols. of (I) are needed to liberate 1 mol. of chlorophyll-*a* when up to one sixth of the dye is liberated; complete liberation of the dye requires much more (I). Normal soaps do not affect chloroplastin. The carotene of yellow carrots is present as symplex in non-extractable form but is at once liberated by 1—1·5% invert soap solutions. Invert soaps do not split chromoproteins. CH_2Ph·NMe_2Br·$C_{12}H_{25}$-n (II) does not ppt., and prevents coagulation of, the yellow enzyme of yeast or of oxyhæmoglobin (III) by heat; its action on (III) is antagonised by Na deoxycholate. Methæmoglobin is pptd. by ~1% invert soap solution. Catalase is unaffected by an equal vol. of 0·1—10% (II) at pH 7·2—5·4, but is pptd. and inactivated by a 1% solution at pH 8·2 (Na_2CO_3). Ferritin (IV) is completely pptd. from 2 c.c. of 0·1% solution by 1 c.c. of a 1 : 300, but not 1 : 350, solution of (II); the (IV) is denatured but the Fe is not liberated; 1 mol. of (II) ppts. 1·03 atom of Fe. Invert soaps ppt. oxyhæmocyanin from dil. Na_2CO_3 (not dil. AcOH), the fresh (not old) ppt. being sol. in an excess of soap or $(NH_4)_2SO_4$ and dissolving also if the original mixture is warmed; Cu is not liberated. Ovoverdin is split by 0·00005% invert soap solution (colour change to the red of astaxanthin), but pptn. of the protein requires 0·0005% soap solution. Gelatins and ovalbumin (V) are pptd. by invert soaps if the pH is such that the protein is present as anion; for proteins having isoelectric point near pH 7·2 the CO_2 content of the solution is important. With (V), SH is liberated before pptn. occurs. The concn. of the soaps required for bactericidal action is approx. that (0·001—0·00002%) required for pptn. of proteins. The action of invert soap on genes resembles that of *X*-rays. Isolation of β-carotene (from carrots) and of lycopene (from tomatoes) is described. R. S. C.

Crystalline muscle phosphorylase.—See A., 1944, III, 218.

X.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Lignin and related compounds. LXIII. Ultra-violet absorption spectra of ethanol lignins. R. F. Patterson and H. Hibbert (*J. Amer. Chem. Soc.*, 1943, **65**, 1869—1873; cf. A., 1943, II, 346).—Absorption spectra are recorded for the fractions of spruce and maple lignins and for ethanolysis products from OH·CHMe·COAr and OH·$[CH_2]_2$·COAr (Ar = vanillyl). Comparisons with those of known ingredients and related compounds (*loc. cit.*) confirm the aromatic nature of lignin, the existence of OH-derivatives of 4 : 3 : 1-OH·C_6H_3(OMe)·COEt in both lignins and of 4 : 3 : 5 : 1-OH·C_6H_2(OMe)$_2$·COEt in spruce lignin, and conjugation (to an unkown extent) between the aryl nucleus and the side-chain. R. S. C.

Lignin. XII. Sulphite liquor from beech wood. H. Friese and G. Stoeck [with, in part, R. Konau] (*Ber.*, 1940, **73**, [*B*], 1135—1145; cf. A., 1938, II, 331).—The liquor is repeatedly evaporated with H_2O under diminished pressure to remove volatile acids and taken to dryness after neutralisation with $CaCO_3$. Treatment with boiling EtOH and MeOH gives pure *d*-xylose (I), isolable by direct crystallisation. The non-cryst. residue in acetylated to a protein sol. in $CHCl_3$ and H_2O but not in Et_2O and containing ~36% OAc with Ca, S, and OMe, and an Et_2O-sol. fraction free from Ca and S but containing 71·8% OAc and 2·1% OMe. Hydrolysis gives (I) and fermentable hexoses, mainly mannose. Glucose is probably present. Methylpentoses, ketoses, uronic acids, and, probably, arabinose and galactose are absent. (I) frequently contains OMe in non-glucosidic union. The extractions remove sugars almost quantitatively. Their amount is 26—30% of the dry residue but depends on the boiling. (I) constitutes ~76% of the free carbohydrates. The remaining portion of the alcoholic extract separable by acetylation is a *lignin–carbohydrate* compound (Ca 4·2, S 6·5, OMe 11·0, OAc 36·5, C 45·2, H 4·7%). Extraction of the residue from the alcoholic extractions with 80% MeOH gives a brown solid (25—35% of the initial material, dependent on the duration of boiling). It contains Ca 6, S 6, OMe 11% and gives only small amounts of sugar acetates when drastically treated. The residue from the acetylation is a pale brown lignin–carbohydrate compound which contains little combined lignin. Hydrolysis with dil. H_2SO_4 is incomplete but sulphacetolysis leads to Et_2O-sol. sugar acetates with OAc 68·8, OMe 2·34% but no Ca or S. Ultrafiltration of the remaining material leaves a brown powder with C 52 H 4·7, OMe 16, S 5·1, and Ca 4·0%. The ultrafiltrate on pptn. with MeOH gives a substance with C 41·7, H 5·1, OMe 10·5, S 7·3, and Ca 8·5%; the MeOH contains $Ca(OAc)_2$, $(HCO_2)_2Ca$, and small amounts of Ca ligninsulphonate. H. W.

Oxidative degradation of pectin in aqueous solution. Viscosimetric determinations. H. Deuel (*Helv. Chim. Acta*, 1943, **26**, 2002—2025).—The irreversible oxidative degradation of pectin (I) in aq. solution is followed viscosimetrically. Ascorbic acid (II) and similar enediols degrade (I) in the presence of O_2, the change being accelerated by increase of temp., and occurring most rapidly at the neutral point. Decomp. of (I) and oxidation of (II) are inter-related. Dehydroascorbic acid has a weak degrading action. At room temp. H_2O_2 in small concn. causes decomp. of the mol. of (I); increase of temp. causes very marked acceleration; this degradation occurs more rapidly in the presence of (II), Fe^{II} salts, N_2H_4, and NH_2OH. The oxidation of (I) is decelerated by EtOH and sucrose and inhibited by H_2S, SO_2, and I. The degradation of (I) described above is externally similar to hydrolysis by pectinase and oxidative decomp. by HIO_4 but the reaction mechanism is different. Activated H_2O_2 and autoxidising (II) degrade the most varied carbohydrates on addition to (I). H. W.

Gliotoxin, the antibiotic principle of *Gliocladium fimbriatum*. I. Production, physical and biological properties. J. R. Johnson, W. F. Bruce, and J. D. Dutcher (*J. Amer. Chem. Soc.*, 1943, **65**, 2005—2009).—Prep. of gliotoxin, new formula $C_{13}H_{14}O_4N_2S_2$, $[\alpha]_D^{25}$ −290 ± 10° in EtOH, −270° ± 10° in C_5H_5N, −255 ± 10° in $CHCl_3$, +111° → 0° in 5 days in NaOH–EtOH–H_2O, is described. The mol. wt. is best determined cryoscopically in $NHPh_2$, other solvents giving erroneous or erratic results. Crystallo-optical properties and solubilities [much the greatest in C_5H_5N (at 100°) or dioxan] in 16 solvents are described. The absorption spectrum (detailed) resembles that of indole and tryptophan, indicating presence of an indole nucleus. For physiological properties see A., 1944, III, 292. R. S. C.

Formation of a nicotinamide-like substance from various amino-acids and related compounds. M. R. Bovarnick (*J. Biol. Chem.*, 1943, **151**, 467—475).—The reaction between asparagine (I) and glutamic acid (II) that results in the formation of a nicotinamide-like substance (III) is catalysed by Mn (best; 10 times amount of (III)] and Fe salts (Mg, Ca, Al, Cr, Co, Ni, and Cu have little effect), and is promoted by aeration. Certain NH_2-acids and non-N dibasic acids are capable of substituting for (II) in the reaction. In order of decreasing activity are methionine [as active as (II)], proline, citrulline, ornithine, α-ketoglutaric acid, glutaric acid, maleic acid, arginine, phenylalanine, hydroxyproline, fumaric acid, tyrosine, oxalacetic acid, lysine, serine, threonine, and malic acid. All the terminal-substituted C_5 NH_2-acids react. The only effective substitute for (I) is glutamine. The NH_4 salts of aspartic, α-ketoglutaric, maleic, and malic acids when heated with (II) produce small amounts of nicotinamide activity, although their Na salts are inactive. With many mixtures of (I) + NH_2-acid, much more activity is produced by treating with H_2O_2 for 2 days at room temp., then autoclaving (15 min.), than at 100° (48 hr.); also small amounts of nicotinamide activity are produced from many NH_2-acids and from the NH_4 salts of several dicarboxylic acids by H_2O_2 alone, in absence of (I) and (II). Reaction mechanisms are discussed. A. T. P.

Hypericin and a non-fluorescent, photosensitive pigment from St. John's wort (*Hypericum perforatum*).—See A., 1944, III, 232.

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A II—Organic Chemistry.

MAY, 1944.

I.—ALIPHATIC.

Separation and purification of organic compounds by filtration of the molten eutectics. L. Kofler and R. Wannenmacher (*Ber.*, 1940, 73, [*B*], 1388—1391).—A thin layer of the mixture is spread evenly over a piece of hardened filter-paper, ~18 × 18 mm., placed on an object glass over which a second object glass is firmly placed. The arrangement is heated in the micro-m.p. apparatus to a temp. between that of the beginning and end of the melting of the mixture (determined previously). The upper object glass is then pressed firmly on to the mixture and removed, generally bringing the unmelted crystals on its under side. The filter-paper is changed and the whole operation is repeated several times at a temp. gradually increased to that above the point of primary crystallisation. Hardened paper is useful only at >200°, above which thin porous platelets are used. The possibility of the presence of a third component in a mixture in which two substances are known to be present is examined by determining the eutectic temp. of a synthetic mixture of the two substances under the microscope; its identity with that of the mixture under examination is evidence against the presence of further compounds, which can be strengthened if the eutectic temp. remains unchanged when a mixture of the two mixtures is used. If the two components form a mol. mixture either it or one of the components is obtained according to the relative amounts of the substances which are present. H. W.

Catalytic dehydrogenation of hydrocarbons and its application to the synthesis of rubber from gases. A. A. Balandin (*Bull. Acad. Sci. U.R.S.S.*, 1942, *Cl. Sci. chim.*, 21—44).—Dehydrogenation of hydrocarbons is considered from the point of view of the author's multiplet theory. The results of experimental work, published elsewhere, on the conversion of *n*-C_4H_{10} into C_4H_8 (B., 1943, II, 101), Δ^α-C_4H_8 into C_4H_6 (B., 1942, II, 417, and *infra*), and PhEt into styrene over Cr_2O_3 and other catalysts are discussed. R. C. P.

Catalytic dehydrogenation of butylene to butadiene at reduced pressure. A. A. Balandin, N. D. Zelinski, O. K. Bogdanova, and A. P. Schtscheglova (*J. Appl. Chem. Russ.*, 1942, **15**, 128—138).—Δ^α-Butene (**I**) passed through an unspecified catalyst gives *s*-butadiene; the yield is up to 85% on the (**I**) consumed and up to 29% on the (**I**) passed through; the best temp. is 580—600°. The yield of $(CH_2{:}CH)_2$ is almost independent of the rate of gas flow and nearly as high as corresponds to the equilibrium concn. A few % of (**I**) are isomerised to Δ^β-butene, and a few % of C are formed. J. J. B.

Commercial alkylation with hydrogen fluoride catalyst.—See B., 1944, II, 61.

Chlorination of gaseous unsaturated compounds.—See B., 1944, II, 62

[Catalytic] reaction of sulphur dioxide with olefines. Ceiling-temperature phenomena.—See A., 1944, I, 108.

Stereoisomerism of unsaturated compounds. VII. Diastereoisomeric dibromides. W. G. Young, S. J. Cristol, and T. Skei (*J. Amer. Chem. Soc.*, 1943, **65**, 2099—2102; cf. A., 1943, II, 290).—*meso*- and *dl*-$(CHEt{\cdot}OH)_2$ with $Ac_2O + H_2SO_4$ (few drops) give *meso*-, b.p. 83·3—83·7°/5·5 mm., and *dl*-diacetates, b.p. 88·0—88·4°/5·5 mm., and thence (65% HBr; room temp.; 1 week) *meso*- (**I**), b.p. 70·1—70·3°/9 mm., and *dl*-$(CHEtBr)_2$ (**II**), b.p. 72·1—72·5°/9 mm., respectively. Rates of reaction with KI in 99% MeOH at 75° and 60° give heats of activation as follows: *dl-threo*- 25·7 and *dl-erythro*-CHMeBr·CHEtBr 25·66, (**I**) 25·10, (**II**) 26·60, *dl*- (**III**) 24·40 and *meso*-CHEtBr·$CHBu^\alpha$Br 25·25. *k* differ markedly for the isomerides and are used for identification. The rule that *meso*- have higher heats of activation than *dl*-isomerides (A., 1939, II, 399) does not hold for the C_8-compounds. The steps, glycol → diacetate → (inversion) dibromides, are proved by *k* for the crude products to proceed without formation of stereoisomerides in the C_6- and C_8-series. The reactions, dibromide + Zn-Cu couple in boiling 96% EtOH → olefine → dibromide, are proved similarly to involve formation of 6·4% of diastereoisomeride from (**II**) and 19·5% from (**III**); these and earlier results (*loc. cit.*; A., 1936, 310; Lucas *et al.*, A., 1941, II, 84) show that the amount of rearrangement increases with the length of the chain; this may be due to the slower reaction of the higher dibromides allowing longer time of contact of the olefine with $ZnBr_2$. R. S. C.

Catalysed hydrobromination of unsaturated organic compounds.—See B., 1944, II, 62.

***n*-Butanol and acetone.**—See B., 1944, II, 61.

Acetylene derivatives. XXIV. Halogen derivatives of vinylethinylcarbinols. I. N. Nazarov and J. M. Janbikov (*Bull. Acad. Sci. U.R.S.S.*, 1942, *Cl. Sci. chim.*, 66—79).—The carbinol $CRR'X{\cdot}C{\cdot}C{\cdot}CH{:}CH_2$ [R = R′ = Me, X = OH (**I**)] gives with dry HCl, PCl_3, and $SOCl_2$ the corresponding *chloride* (**II**), b.p. 31—32°/10 mm., with PBr_3 the *bromide*, b.p. 55—56°/17 mm., and with conc. HI the *iodide*, b.p. 65°/6 mm. (crude product explodes above 120°). Treatment of similar carbinols with HCl gas yields the *compounds* (R = Me, R′ = Et, X = Cl), b.p. 46·5—48°/8 mm., (R = Me, R′ = Pr, X = Cl), b.p. 61·5—63°/9 mm., (R = R′ = Et, X = Cl), b.p. 59—61°/7 mm. These monohalogeno-derivatives react with $AgNO_3$ and revert to the carbinols when shaken with aq. KOH, but do not polymerise. (**I**) shaken with conc. HBr, at room temp. yields a mixture containing a *dibromide*, $C_7H_{10}Br_2$, b.p. 92—93°/6 mm., and a monobromide which is stable to alkali and polymerises readily. Agitation of (**II**) with 1% of Cu_2Cl_2 + 0·1% of NH_4Cl at room temp. yields a complex mixture containing $CH_2{:}CH{\cdot}C{:}C{\cdot}CMe{:}CH_2$ (**III**), *δ-chloro-β-methyl-*$\Delta^{\alpha\gamma\epsilon}$*-hexatriene* (**IV**), b.p. 38—40°/9 mm. (stable to $AgNO_3$ and aq. KOH, polymerises on keeping), a *dichloride*, $C_7H_{10}Cl_2$ (**V**), b.p. 64—65°/6 mm., and probably $CMe_2{:}C{:}CCl{\cdot}CH{:}CH_2$. (**III**) with conc. HCl at room temp. gives δζ-dichloro-β-methyl-$\Delta^{\beta\delta}$-hexadiene, b.p. 72—73°/9 mm., and with an insufficiency of HCl, a *monochloride*, C_7H_9Cl, b.p. 39—41°/14 mm. (reacts with $AgNO_3$, does not polymerise). (**III**) with conc. HCl, Cu_2Cl_2, and NH_4Cl yields mono- and di-chlorides probably identical with (**IV**) and (**V**). R. C. P.

Stereoisomerism of the leaf alcohol, natural Δ^γ-hexenol. M. Stoll and A. Rouve (*Ber.*, 1940, 73, [*B*], 1358—1360).—In reply to Takei *et al.* (A., 1940, II, 335) it is pointed out that the assignment of the *cis*-configuration to the hexenol obtained by reduction (colloidal Pd) of Δ^γ-hexinol (and hence the configuration of the natural leaf alcohol) depends on the universality of the observations of Bourguel (A., 1930, 317) and is not affected by conflicting results obtained by different methods and with other catalysts. H. W.

Racemisation accompanying molecular rearrangements. P. G. Stevens and S. H. J. Greenwood (*J. Amer. Chem. Soc.*, 1943, **65**, 2153—2156).—*d*-$CHMePr^\alpha{\cdot}CO_2H$ (prep. from the *dl*-acid by cinchonidine), b.p. 84·5°/9 mm., $[\alpha]_D^{25}$ +7·1°, and CH_2N_2 give the Me ester, b.p. 77°/98·5 mm., $[\alpha]_D^{25}$ +9·1°, converted by MgMeI at 0° and then room temp. and finally aq. NH_4Cl into *l*-$CHMePr^\alpha{\cdot}CMe_2{\cdot}OH$, b.p. 75°/29 mm., $[\alpha]_D^5$ −17·7°. With conc. HCl this gives a 1 : 1 *dl*-mixture (*A*) of $CHMePr^\alpha CMe_2Cl$ (**I**) and $CMePr^\alpha Pr^\beta Cl$ (**II**), hydrolysed to *dl*-$CHMePr^\alpha{\cdot}CMe_2{\cdot}OH$ (**III**) (*phenylurethane*, m.p. 74°) and *dl*-$CMePr^\alpha Pr^\beta{\cdot}OH$ (**IV**) (*phenylurethane*, m.p. 90·5°). A similar mixture (*A*) is obtained from either (**III**) or (**IV**) by conc. HCl. *d*-$CHPr^\alpha Bu^\gamma{\cdot}OH$ and conc. HCl give 6% of *l*-$CHPr^\alpha Bu^\gamma Cl$, $[\alpha]_D$ −14°, and 47% each of (**I**) and (**II**). *l*-$CHPr^\alpha Bu^\gamma{\cdot}OH$ and conc. HCl give 94·2% of *d*-(**I**) (cf. A., 1939, II, 2). R. S. C.

Preparation of pentaerythritol.—See B., 1944, II, 62.

Acetolysis of trimethylene-*D*-mannitol. βε-Methylene-*D*-mannitol. A. T. Ness, R. M. Hann, and C. S. Hudson (*J. Amer. Chem. Soc.*, 1943, **65**, 2215—2222).—Structures given below are proved by the reactions described. αγ-δζ-Dimethylenedulcitol βε-dibenzoate in H_2SO_4–Ac_2O–AcOH at 25° gives (?) *γδ-diacetoxymethyldulcitol βε-dibenzoate αζ-diacetate*, m.p. 87—88° (consumes 6 NaOH), hydrolysed by NaOMe–MeOH in $CHCl_3$ at room temp. to dulcitol (83%) and CH_2O (1·83 mols.). αγ-δζ-Dimethylenedulcitol βε-diacetate gives similarly (?) *γδ-diacetoxymethyldulcitol αβεζ-tetra-acetate* (76%), m.p. 93—94°. The "mannitol triformacetal of Schulz and Tollens (A., 1894, i, 438; 1896, i, 115) is *αγ-βε-δζ-trimethylene*-D-*mannitol* (**I**), m.p. 232—233° (corr.), $[\alpha]_D^{20}$ −104·2° in $CHCl_3$; its prep. is improved to give a 94% yield; under other conditions αγ-δζ- or αγ-εζ-dimethylene-*D*-manmtol (**II**), m.p. 204—208° (corr), $[\alpha]_D^{20}$ −91·0° in H_2O, is also obtained. With CH_2O–conc. HCl at 50° (**II**) rapidly gives (**I**). In H_2SO_4–Ac_2O–AcOH, (**I**) gives *γδ-diacetoxymethyl-βε-methylene*-D-*mannitol αζ-diacetate* (81%), m.p. 129—

130°, $[\alpha]_D^{20}$ +57·6° in $CHCl_3$, hydrolysed by NaOMe–MeOH in $CHCl_3$ to *βε-methylene*-D-*mannitol* (**III**), m.p. 173—174° (corr.), $[\alpha]_D^{20}$ −51·4° in H_2O [*tetra-acetate*, m.p. 117—118°, $[\alpha]_D^{20}$ −1·3° in $CHCl_3$, *-benzoate*, m.p. 107—109°, $[\alpha]_D^{20}$ −7·5° in $CHCl_3$, and *-p-toluenesulphonate*, m.p. 177—178° (corr.), $[\alpha]_D^{20}$ +3·5° in $CHCl_3$]. (**III**) consumes 1·07 equivs. of $Pb(OAc)_4$ in AcOH and 1·10—1·14 equivs. of aq. $NaIO_4$ (giving no CH_2O or acid). With aq. HIO_4, (**III**) gives methylene-bis-2-*D*-glycerose (**IV**), $CH_2[O{\cdot}CH(CH_2{\cdot}OH){\cdot}CHO]_2$, $[\alpha]_D^{20}$ +10·5° in H_2O, hydrogenated (Raney Ni; room temp./133 atm.) *in situ* to *methylenebis-β-glycerol*, m.p. 85—86° (*tetrabenzoate*, m.p. 69—71°), which in 2N-H_2SO_4 at room temp. and then the b.p. gives glycerol and CH_2O. With 2 mols. of BzCl in C_5H_5N at 0° and then 20°, (**III**) gives *βε-methylene*-D-*mannitol αζ-dibenzoate* (**V**), m.p. 119—120°, $[\alpha]_D^{20}$ −70·3° in $CHCl_3$, which consumes 4·92 equivs. of $Pb(OAc)_4$ in AcOH but with 1·1 equivs. and then $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$ gives the *disemicarbazone dibenzoate*, m.p. 193—195° (corr.), $[\alpha]_D$ +83·6° in AcOH, of (**IV**). With PhCHO and $ZnCl_2$ at room temp., (**V**) gives *γδ-benzylidene-βε-methylene*-D-*mannitol αζ-dibenzoate*, m.p. 151—152°, $[\alpha]_D^{20}$ +61·2° in $CHCl_3$, also obtained from γδ-benzylidene-*D*-mannitol αζ-dibenzoate, paraformaldehyde, and $CaSO_4$ in C_6H_6 at 150°. Treating (**IV**) in solution with acid, neutralising, and hydrogenating (Raney Ni) gives *5-hydroxy-4 : 4 : 6-tri(hydroxymethyl)-1 : 3-dioxan*, m.p. 139—140°, $[\alpha]_D^{20}$ +39·7° in H_2O (*tetra-acetate*, m.p. 94—94°, $[\alpha]_D^{20}$ +12·4° in $CHCl_3$, +20·4° in $COMe_2$). R. S. C.

Dibenzoates of sorbitol and mannitol and their methylene derivatives. W. N. Haworth and L. F. Wiggins (*J.C.S.*, 1944, 58—61).—Sorbitol αζ-dibenzoate gives *dimethylenesorbitol αζ-dibenzoate*, m.p. 160°, $[\alpha]_D^{19}$ +22·7° in $CHCl_3$, which gives *βγδε-dimethylenesorbitol* (**I**), m.p. 192—193°, $[\alpha]_D^{8}$ +42·5° in H_2O. Oxidation of (**I**) (CrO_3 in AcOH) gives dimethyleneglucosaccharic acid and a dimethylene-hexonic acid, showing the Bz groups to have been at $C_{(\alpha)}$ and $C_{(\zeta)}$, and CH_2 radicals at $C_{(\beta)}$, $C_{(\gamma)}$, $C_{(\delta)}$, and $C_{(\epsilon)}$, though exact structure is not determined. (**I**) gives *αζ-dichloro-*, m.p. 116—118°, $[\alpha]_D^{15}$ +20·0° in $CHCl_3$, *αζ-ditriphenylmethyl-*, m.p. 209—210°, $[\alpha]_D^{8}$ +12·0° in $CHCl_3$, *αζ-di-p-toluenesulphonyl-*, m.p. 102—103°, $[\alpha]_D^{23}$ +5·4° in $CHCl_3$, and *αζ-dimethyl-dimethylenesorbitol*, m.p. 43°, $[\alpha]^{17}$ +9·4° in $CHCl_3$. Mannitol gives a similar series: *dimethylenemannitol αζ-dibenzoate*, m.p. 121°, $[\alpha]_D^{1}$ +51·2° in $CHCl_3$, and *monomethylene-mannitol αζ-dibenzoate*, m.p. 154° $[\alpha]^{17}$ +25·0° in $CHCl_3$; *βγ-δε-dimethylenemannitol*, m.p. 138—139°, $[\alpha]^{16}$ +70·5° in H_2O; *αζ-dimethyl-*, m.p. 65·5°, $[\alpha]_D^{9}$ +74·9° in $CHCl_3$, and *αζ-ditriphenylmethyl-βγ-δε-dimethylenemannitol*, m.p. 210°, $[\alpha]_D^{18}$ +24·0° in $CHCl_3$. D. G.

Manufacture of vinyl ethers.—See B., 1944, II, 62.

Reactions of carboxylic acids in aqueous solution. P. S. MacMahon and T. N. Srivastava (*J. Indian Chem. Soc.*, 1943, **20**, 307—311).—$HgCl_2$ is unsuitable as a reagent because of formation of complexes. The reduction of $HAuCl_4$ (**I**) by oxalic (**II**), citric (**III**), malic (**IV**), tartaric (**V**), and malonic (**VI**) acid is not accompanied by formation of H_2O_2, is retarded by NaCl and KCl, and is accelerated by light [except for (**VI**)], O_2 [except for (**II**)], temp., concn. of acid, and small amounts of $KMnO_4$ [except for (**II**)]; the last effect is a max. if (**I**) is added last, immediately after the $KMnO_4$ is decolorised; the effect gradually diminishes as the period between the additions is increased, but is still appreciable after 14 days. This enhanced reducing power, hitherto ascribed to chemical induction, is [except for (**II**)] due to intermediate oxidation products, shown to be $CO(CH_2{\cdot}CO_2H)_2$ from (**III**), possibly $[C(OH){\cdot}CO_2H]_2$ from (**V**), and not to be $CO_2H{\cdot}CH{:}C(OH){\cdot}CO_2H$ from (**IV**). "After-effects" following photobromination of (**IV**) are due to an impurity, and are not shown by the pure acid; of (**III**), are due to $CBr_3{\cdot}CO{\cdot}CHBr_2$; and of (**V**) to an oxidation product, possibly aldehydotartronic acid or an isomeride. S. A. M.

Application of the isotopic method to the investigation of the mechanism of chemical reactions. III. Mechanism of the reaction of acid anhydrides with alcohols. N. I. Dedusenko and A. E. Brodski (*Acta Physicochi n. U.R.S.S.*, 1942, **17**, 314—318).—Acylation with Ac_2O of EtOH having a high content of ^{18}O affords evidence that the reaction proceeds according to $EtO{:}H + AcO{\cdot}Ac \rightarrow EtO{\cdot}Ac + AcO{\cdot}H$ and not according to $Et{:}OH + Ac{\cdot}OAc \rightarrow Et{\cdot}OAc + Ac{\cdot}OH$, where points of formation are indicated by dots. Heavy EtOH was prepared by fractional distillation of ordinary EtOH. C. R. H.

Palladium-synthetic high polymer catalysts.—See A., 1944, I, 109.

Solidification point curves of binary [fatty] acid mixtures.—See A., 1944, I, 104.

Synthesis of Δ⁹- and Δ¹⁰-octadecenoic acids. R. Kapp and A. Knoll (*J. Amer. Chem. Soc.*, 1943, **65**, 2062—2064).—Condensing $CO_2Et{\cdot}CHAc{\cdot}[CH_2]_8{\cdot}CO_2Et$, b.p. 164—165°/4·5 mm., with $CH_2{:}CH{\cdot}[CH_2]_8{\cdot}COCl$, b.p. 127·5—128°/13 mm., and boiling the product with, successively, 4% KOH, 5% H_2SO_4, and 5% NaOH gives *η-keto-Δ¹⁰-octadecenoic acid* (28%), m.p. 72·2—73° (*semicarbazone*, m.p. 102·5—103°), reduced by N_2H_4,HCl–NaOEt–EtOH at 185—200° to *Δ¹⁰-octadecenoic acid* (65%), m.p. 55—55·5°, which with $KMnO_4$–$COMe_2$ gives $[CH_2]_{13}(CO_2H)_2$, m.p. 118°.
$CHMe{:}CH{\cdot}[CH_2]_8{\cdot}COCl$, b.p. 112—113°/4 mm., leads similarly to *η-keto-Δ⁹-octadecenoic acid* (23%), m.p. 78·4—78·9° (*semicarbazone*, m.p. 112·8—113·5°), and thence *Δ⁹-octadecenoic acid*, m.p. 62·8—63·5°, which with $KMnO_4$ gives $[CH_2]_{12}(CO_2H)_2$, m.p. 124—124·2°. M.p. are corr. R. S. C.

Unsaturated synthetic glycerides. I. Unsymmetrical monooleo-disaturated triglycerides. B. F. Daubert, H. H. Fricke, and H. E. Longenecker. **II. Unsymmetrical dioleo-monosaturated triglycerides.** B. F. Daubert, C. J. Spiegl, and H. E. Longenecker (*J. Amer. Chem. Soc.*, 1943, **65**, 2142—2144, 2144—2145).—I. Boiling oleic acid with $(COCl)_2$ with removal of H_2O gives oleyl chloride (**I**) (90%), b.p. 163°/2 mm. *iso*Propylideneglycerol with (**I**) in quinoline–$CHCl_3$ at room temp. and then conc. HCl–Et_2O gives *α-mono-olein*, m.p. 35·5° (lit. an impure oil), converted by RCOCl in quinoline–$CHCl_3$ at 45° into *glyceryl α-oleate βγ-di-n-decoate*, m.p. 3—4°, *-n-dodecoate*, m.p. 20·0°, *-myristate*, m.p. 25·0°, *-palmitate*, m.p. 34·5°, and *-stearate*, m.p. 38·5°. Hydrogenation (Pd-black; EtOH; 20 lb.) then gives glyceryl α-stearate βγ-didecoate, m.p. 44°, βγ-didodecoate, m.p. 45·2°, βγ-di-*n*-myristate, m.p. 57·0° and βγ-dipalmitate, m.p. 63·0°.
II. α-Acylglycerol and (**I**) in quinoline–$CHCl_3$ at the b.p. give *glyceryl αβ-dioleate γ-n-hexoate*, m.p. −11·0° to −10·0°, *γ-n-octoate*, m.p. −6·6° to −5·6°, *γ-n-decoate*, m.p. −0·8° to 0·5°, *γ-n-dodecoate*, m.p. 5·5—6·5°, *γ-myristate*, m.p. 12·5—13·5°, *γ-palmitate*, m.p. 18·0—19·0°, and *γ-stearate*, m.p. 22·5—23·5°, whence hydrogenation as above yields glyceryl αβ-distearate *γ-n*-hexoate, m.p. 44·0°, *γ-n*-octoate, m.p. 47·5°, *γ-n*-decoate, m.p. 47·8°, γ-myristate, m.p. 58·2°, and γ-palmitate, m.p. 62·3°. R. S. C.

Oxidation of oxalic acid solutions by elementary oxygen in presence of manganese.—See A., 1944, I, 107.

***N*-Nitrosoacylarylamides as catalysts in addition polymerisation.** A. T. Blomquist, J. R. Johnson, and H. J. Sykes (*J. Amer. Chem. Soc.*, 1943, **65**, 2446—2448).—Mixed polymers are formed (i) when $CH_2{:}CHPh$ is kept in the dark in presence of *p*-$C_6H_4Br{\cdot}NAc{\cdot}NO$ (**I**) at room temp. or of *NN'-dinitrososuccindi-*p*-bromoanilide*, m.p. 116°, at 27° (N_2), (ii) when $CH_2{:}CMe{\cdot}CO_2Me$ is kept at 26° with (**I**), *α-bromo-N-nitrosoisovaleranilide* (**II**), m.p. 59°, or *N-nitroso-m-bromobenzanilide* (**III**), m.p. 61° (gives also a little *m*-$C_6H_4Br{\cdot}CO_2H$), or (iii) $CH_2{:}CH{\cdot}CN$ is kept with (**I**) at 60—70°, or at room temp. with (**II**) in light petroleum, or at 27—30° with (**III**) in C_6H_6. The polymers contain Br when the Ar, but not the R, of $NO{\cdot}NAr{\cdot}COR$ contains Br. This indicates decomp. as follows: $NO{\cdot}NAr{\cdot}COR \leftrightarrow ArN{:}N{\cdot}O{\cdot}COR \rightarrow N_2 + Ar{\cdot} + RCO_2{\cdot}$; $RCO_2{\cdot}$ is not incorporated into the polymer chain. The NO-compounds are prepared by adding NOCl–Ac_2O to NHAr·COR, KOAc, and P_2O_5 in AcOH–Ac_2O at 7° and keeping at 7—12° for 2 hr. *NN'-Dinitrosofumardianilide*, m.p. 121° (explosive decomp.), and *NN'-dinitrososuccin-di-*p*-chloroanilide*, m.p. 95°, -dianilide, m.p. 111° and 137°, and *-di-β-naphthalide*, m.p. 118°, and *αα'-dibromo-NN'-dinitrososuccindianilide*, m.p. 110°, are also described. R. S. C.

Condensations. XX. Acetoacetic ester condensations effected by means of sodium or potassium amide and magnesium *iso*propyl bromide. J. C. Shivers, B. E. Hudson, jun., and C. R. Hauser (*J. Amer. Chem. Soc.*, 1943, **65**, 2051—2053; cf. A., 1943, II, 216).—With KNH_2 in liquid NH_3, EtOAc gives only 5—10% of $CH_3Ac{\cdot}CO_2Et$ (cf. Titherly, *J.C.S.*, 1902, **81**, 1520; Freund *et al.*, A., 1902, i, 584). Adding $CH_2Ph{\cdot}CO_2Et$ to KNH_2–Et_2O (prep. described) at room temp. and then boiling gives 97% (calc. on KNH_2) of $CH_2Ph{\cdot}CO{\cdot}CHPh{\cdot}CO_2Et$. In presence of $NaNH_2$–Et_2O $Bu^{\gamma}OAc$ gives 57% and in presence of $MgPr^{\beta}Br$–Et_2O gives up to 42% of $CH_3Ac{\cdot}CO_2Bu^{\gamma}$, b.p. 75—78°/15 mm. (*semicarbazone*, m.p. 153°). In presence of KNH_2, $Bu^{\beta}CO_2Bu^{\gamma}$ gives 11% and in presence of $MgPr^{\beta}Br$ gives 29% of $Bu^{\beta}CO{\cdot}O{\cdot}CHPr^{\beta}{\cdot}CO_2Bu^{\gamma}$, b.p. 125—126°/15 mm., with some unchanged ester. No condensation of $Pr^{\beta}CO_2Bu^{\gamma}$ occurs in presence of $MgPr^{\beta}Br$. R. S. C.

Rotation dispersion and configuration of α-hydroxy-acids.—See A., 1944, I, 98.

Fatty acid mono-esters of *l*-ascorbic acid and *d-iso*ascorbic acid. D. Swern, A. J. Stirton, J. Turer, and P. A. Wells (*Oil and Soap*, 1943, **20**, 224—226).—Pure *mono-esters* of *l*-ascorbic (**I**) and *d-iso*-ascorbic acid (**II**) with lauric, myristic, palmitic, and stearic acids (m.p. of anhyd. *l*-ascorbyl esters 105·5—106·5°, 110·5—111·5°, 116—117°, and 117·5—118° respectively, and of the d-*iso*ascorbyl series 78—79°, 84—85°, 88·5—89·5°, 91·5—92·5°) have been prepared in 40—50% yields by interaction of the (**I**) or (**II**) with the fatty acid at room temp. in conc. H_2SO_4. The white cryst. products are sol. in most org. solvents (but not light petroleum), and in fats and oils on gently warming; they are mono-esters, reaction having occurred probably at the primary $C_{(6)}$-OH. E. L.

Effect of *X*-rays on ascorbic acid.—See A., 1944, III, 284.

Constitution and detection of hibiscic acid. C. Griebel (*Z. Unters. Lebensm.*, 1942, **83**, 481—586; cf. B., 1939, 993).—Hibiscic acid (**I**), $[\alpha]_D^{20}$ +122° in H_2O, is the *d*(+)-component of *dl-allo*hydroxycitrolactone. The acid obtained on opening the lactone ring has $[\alpha]_D$ +31° in H_2O. Red grapes contain an optically active lactone not identical with (**I**). (**I**) is detected as Pb salt (needles), by titration

(before and after opening of the lactone ring), and by measuring change in $[\alpha]_D$ produced on opening the lactone ring. Tartaric acid interferes. W. McC.

Derivatives of glucosaccharic acid. W. N. Haworth and W. G. M. Jones (*J.C.S.*, 1944, 65—67).—K H glucosaccharate (modified prep. given), with CH_2O and HCl, gives methyleneglucosaccharolactone (I), m.p. 144—146° (hydrate), 165° (anhyd.), $[\alpha]_D^{17}$ +118° in H_2O. (I) with EtOH and a little HCl gives *monomethyleneglucosaccharolactone Et ester*, m.p. 195—197°, but with boiling 4% HCl–MeOH gives Me_2 *monomethyleneglucosaccharate* (II), m.p. 166°, $[\alpha]_D$ +22·6° in H_2O. With NH_3 and H_2O (II) gives *monomethyleneglucosaccharodiamide*, m.p. 235°, and on heating (175°) (II) gives *monomethyleneglucosaccharolactone Me ester*, m.p. 214°. (II) with paraformaldehyde and H_2SO_4 gives Me_2 dimethyleneglucosaccharate, m.p. 157°, and with paracetaldehyde and H_2SO_4 gives *Me*, *monomethylenemonoethylideneglucosaccharate*, m.p. 153°, $[\alpha]_D$ +25·5° in $CHCl_3$. The $CaCl_2$ compound (III) of Et_2 glucosaccharate gives (PhCHO and $ZnCl_2$) Et_2 *monobenzylideneglucosaccharate*, m.p. 124°, $[\alpha]_D$ +36·6° in $CHCl_3$. With $COMe_2$ and $ZnCl_2$ (III) gives Et_2 *isopropylideneglucosaccharate*, b.p. 150° (bath)/0·005 mm., giving *isopropylideneglucosaccharodiamide*, m.p. 184°. With paracetaldehyde and $ZnCl_2$, (III) yields Et_2 *monoethylideneglucosaccharate* (IV), b.p. 165° (bath)/0·023 mm. (IV) gives *monoethylideneglucosaccharodiamide*, m.p. 187°, and $[Ba(OH)_2]$ *monoethylideneglucosaccharolactone*, m.p. 213°, $[\alpha]_D^{18}$ −5·3°. D. G.

Epimerisation of some dimethylenesaccharic acids and their derivatives. W. N. Haworth, W. G. M. Jones, M. Stacey, and L. F. Wiggins (*J.C.S.*, 1944, 61—65).—K H glucosaccharate with paraformaldehyde and H_2SO_4 gives, after esterification, *Me*, *dimethyleneglucosaccharate* (I), m.p. 157·5°. The exact configuration of the CH_2 groups has not yet been determined. At 60°, with $Ba(OH)_2$ and H_2O, (I) gives *dimethyleneglucosaccharic acid* (II), m.p. 223°, $[\alpha]_D^{21}$ +42·5° in H_2O. At 100°, with $Ba(OH)_2$ and H_2O, both (I) and (II) give *dimethylene*-l-*idosaccharic acid* (III), m.p. 292° (decomp.), $[\alpha]_D$ +73·7° in H_2O, which separates in 33% yield as the sparingly sol. Ba salt. (III) with MeOH and HCl gives *Me*, *dimethylene*-l-*idosaccharate*, (IV), m.p. 297°, and with NH_3 and H_2O *dimethylene*-l-*idosaccharodiamide* (V), decomp. 350°. (I) with NH_3 and dry MeOH gives (IV) and with NH_3 and H_2O gives (V). With $Ba(OH)_2$ and H_2O at 100°, (III) gives (II), isolated as (I) in 40% yield. (III) is also obtained from Me_2 dimethylenemannosaccharate with $Ba(OH)_2$ and H_2O at 100°. Tetramethylglucosaccharic acid could not be epimerised under similar conditions. A di-enol form of the saccharic acids is postulated to account for these changes. D. G.

Stabilisation of aldehydes.—See B., 1944, II, 63.

Preparation of aldehydes and ketones by ozone oxidation. A. L. Henne and W. L. Perilstein (*J. Amer. Chem. Soc.*, 1943, **65**, 2183—2185).—Conditions and apparatus (C., 1944, Part 2; cf. A., 1943, II, 252) for ozonolysis and hydrogenation (1% Pd–$CaCO_3$) of the ozonide are described. Yields of ketone or aldehyde are as follows: from $CHBu^a{:}CMe_2$ in MeOH 49%; from n-C_5H_{11}·$CH{:}CHMe$ in EtOAc 8, MeOH 24, or EtOH 37%; from n-C_6H_{13}·$CH{:}CH_2$ in EtOAc 26, MeOH 30, or EtOH 35%; from $CMeBu^a{:}CMe_2$ in EtOAc 61%; from n-C_5H_{11}·$CMe{:}CMe_2$ in EtOAc 44, MeOH 35, or EtOH 40%. *cyclo*Pentene in EtOAc gives $[CH_2]_3(CHO)_2$ (71%); *cyclo*hexene gives $[CH_2]_4(CHO)_2$ (21%). R. S. C.

Interaction of chloral with magnesium *cyclo*hexyl bromide. V. W. Floutz (*J. Amer. Chem. Soc.*, 1943, **65**, 2255).—Adding CCl_3·CHO in Et_2O to Mg *cyclo*hexyl bromide in Et_2O and then boiling gives CCl_3·CH_2·OH (up to 65%) and 1 : 2-dibromo*cyclo*hexane with a little di*cyclo*hexyl. The reverse addition gives slightly better yields. R. S. C.

Kinetics of polymeric aldehydes. XIII. Alteration of the mode of reaction of polyoxymethylene by mechanical pulverisation. J. Löbering and J. Hilber (*Ber.*, 1944, **70**, [*B*], 1382—1388).—Polyoxymethylenes can be subdivided in vibration mills in 20 hr. to the smallest particles of size ~1—3 μ. The microscopic character of the product is unchanged after 90 hr. The mechanical subdivision causes a change in the rate of dissolution which persists after the microscopic appearance has become const. It appears that the mechanical treatment causes a degradation of the polyoxymethylene main valency chains. H. W.

Preparation of primary amines with liquid ammonia. J. von Braun and R. Klar (*Ber.*, 1940, **73**, [*B*], 1417—1419).—The increasing insolubility of alkyl halides with increasing mol. wt. in liquid NH_3 diminishes the suitability of the latter for the prep. of more complex amines. Thus cetyl bromide (I) and liquid NH_3 at 50° give cetylamine, b.p. ~145°/0·15 mm., m.p. 47° (Ac derivative, m.p. 71°), in 45% yield. (I) and $NHEt_2$, which are mutually sol., yield diethylcetylamine, b.p. 161°/0·1 mm., quantitatively. Under similar conditions octadecyl chloride affords octadecylamine, b.p. 164—166°/10 mm., m.p. 47° (*hydrochloride*, m.p. 162°; *picrate*, m.p. 106°; *Ac* derivative, m.p. 68°), in only 35% yield whereas docosyl bromide (II) does not react with liquid NH_3 but with anhyd. $NHMe_2$ affords dimethyldocosylamine, b.p. 190°/0·6 mm., m.p. 44°, quantitatively. This is converted into the methosulphate and then into the quaternary base, which when distilled with conc. alkali affords docosene, b.p. 162°/0·15 mm., m.p. 41°. (II) is transformed by prolonged treatment with a large excess of KCN in aq. $COMe_2$ into *tricosanonitrile*, m.p. 54°, hydrolysed by HCl at 110° to the acid, m.p. 78°. This with HN_3 and H_2SO_4 in $CHCl_3$ gives *docosylamine*, b.p. ~200°/0·5 mm., m.p. 67° (*hydrochloride*; *nitrate*, m.p. 119°; *Ac* derivative, m.p. 88°). H. W.

Manufacture of *iso*butenylamines.—See B., 1944, II, 64.

Crystalline barium acid heparinate. M. L. Wolfrom, D. I. Weisblat, J. V. Karabinos, W. H. McNeely, and J. McLean (*J. Amer. Chem. Soc.*, 1943, **65**, 2077—2085).—Prep. is described of cryst. Ba H heparinate (I), $[\alpha]_D^{26}$ +44° in H_2O (purified by way of the benzidine salt to a product having $[\alpha]_D^{25}$ +47·5° in H_2O), neutral, $[\alpha]_D^{25}$ −15° in H_2O, and Na H mucoitin sulphate, $[\alpha]_D^{5}$ −7·4° in H_2O, and neutral, $[\alpha]_D^{5}$ −24° in H_2O, and Na H chondroitin sulphate, $[\alpha]_D^{25}$ −11·5° in H_2O. Analysis of (I) etc. for C, H, N, and S, anhydrohexuronic acid, and anhydrohexosamine indicates components of (I) to be anhydrohexosamine : anhydrohexuronic acid : SO_3 : Ba = 2·0 : 1·8 : 6·0 : 3·0, but another component may also be present (cf. Charles *et al.*, A., 1936, 1534). (I) may be $C_{24}H_{35}O_{36}N_2S_5Ba_{2\cdot5}$ or $C_{30}H_{42}O_{43}N_2S_5Ba_3$. It contains no NAc, CMe, or NH_2; η excludes a high mol. wt.; the titration curve shows that all the CO_2H of the uronic acid component is free. Hydrolysis gives *D*-glucosamine. The N may be present as $>CH{\cdot}NH{\cdot}CH{\cdot}O{\cdot}\longleftrightarrow>CH{\cdot}N{:}CH{\cdot}$. Na H heparinate consumes a small amount of $NaIO_4$, indicating an equiv. wt. = 1900 for (I). Repeated crystallisation of (I) from dil. AcOH changes the cryst. form (photomicrographs given) and causes inactivation. (I) is also inactivated by long drying at 100° and the Na salt is inactivated by H_2O_2–NH_3. Neither the toluidine-blue test nor the S content is a criterion of activity. Two possible structures are discussed. R. S. C.

ωω′-Dimethionine. H. R. Snyder, E. E. Howe, G. W. Cannon, and M. A. Nyman (*J. Amer. Chem. Soc.*, 1943, **65**, 2211—2214).—*dl*-Methionine (I), prepared by the method of Barger *et al.* (A., 1931, 1279), is accompanied by ~5% of "ψ-methionine" (II), m.p. 285—288°, which is shown to be a mixture of *dl*- and *meso*-ωω′-dimethionine, $\{CH_2{\cdot}S{\cdot}[CH_2]_2{\cdot}CH(NH_2){\cdot}CO_2H\}_2$. (II) gives a green colour with anhyd. $CuSO_4$–H_2SO_4, contains 2 CO_2H and 2 NH_2 (Van Slyke) but no CMe, SMe, or S·S, gives a Ac_2, m.p. 173—174°, Bz_2, m.p. 157—160°, and $(HCO)_2$ derivative, m.p. 114—115°. $(CH_2{\cdot}S{\cdot}[CH_2]_2{\cdot}Cl)_2$ (1 mol.), $NHAc{\cdot}CH(CO_2Et)_2$ (2 mols.), and NaOEt in boiling EtOH give the *ester*, $\{CH_2{\cdot}S{\cdot}[CH_2]_2{\cdot}C(CO_2Et)_2{\cdot}NHAc\}_2$ (25·2%), m.p. 154—155°, converted in boiling NaOH–H_2O–EtOH into (II). PhNCO and (II) give, after ring-closure by HCl, dl- and meso-*ethylene di*-(β-3-*phenyl*-5-*hydantoinyl sulphide*) (69%), m.p. 155—164° (decomp.), reduced (H_2–Raney Ni) to 3-*phenyl*-5-*ethylhydantoin* (75%), m.p. 121—122°, also obtained from (I). H_2O_2–AcOH converts (I) into the *disulphone*, decomp. 325—350° (block), but in Ac_2O–AcOH gives α-*acetamido*-γ-β′-*hydroxyethanesulphonyl*-n-*butyric acid* (61%), darkens 226°, m.p. 231—235° (decomp.; variable), converted by boiling, conc. HCl and then C_5H_5N in 25% EtOH at 0° into α-*amino*-γ-β′-*hydroxyethanesulphonyl*-n-*butyric acid* (III), darkens 250°, decomp. 265—280°. 3 : 6-Di-β-chloroethyl-2 : 5-diketopiperazine, $SH{\cdot}[CH_2]_2{\cdot}OH$, and KOH in boiling EtOH give 3 : 6-*di*-β-β′-*hydroxyethylthiolethyl*- (IV) (53·3%), m.p. 148—149°, and a small amount of 3-β-*chloroethyl*-6-β-β′-*hydroxyethylthiolethyl*-2 : 5-*diketopiperazine*, m.p. 171—178°. Boiling conc. HCl hydrolyses (IV) to impure α-amino-γ-β′-hydroxyethylthiol-n-butyric acid, amorphous, m.p. 275—280° (decomp.), whence (III) is obtained (35·4%) by H_2O_2–AcOH. R. S. C.

Interaction of ethyl diazoacetate with stannic chloride and ferric chloride. A. N. Nesmejanov and A. E. Segalevitsch (*Bull. Acad. Sci. U.R.S.S.*, 1942, *Cl. Sci. chim.*, 8—13).—Interaction of $SnCl_4$ and $CHN_2{\cdot}CO_2Et$ in cold light petroleum yields the *compound*, $[CN_2{:}C(OEt){\cdot}O]_2SnCl_2$. $FeCl_3$ reacts analogously, yielding the *compound*, $CN_2{:}C(OEt){\cdot}O{\cdot}FeCl_2$. At room temp. decomp. of both compounds begins within a few min.; moisture immediately liberates N_2 from them. R. C. P.

II.—SUGARS AND GLUCOSIDES.

Nicotinamide riboside.—See A., 1944, III, 270.

Super-molecular constitution of cellulose. T. Lieser (*Chem.-Ztg.*, 1943, **67**, 197—202).—A review.

Application of the isotopic method to the investigation of chemical reactions. IV. Reaction of xanthation, reaction of cellulose mercerisation, and the structure of alkali-cellulose. I. A. Makolkin (*Acta Physicochim., U.R.S.S.*, 1942, **17**, 319—322; cf. A., 1944, II, 119).—The xanthation of EtOH and cellulose (I) has been investigated using NaOH with a high ^{18}O content. The data show that O from NaOH and not O from EtOH or (I) passes into H_2O, O from these latter passing into xanthate. A similar investigation of the mercerisation of cellulose affords evidence that alkali-cellulose is an additive product of NaOH to cellulose and not an alcoholate. C. R. H.

Steroids. XXXV. Preparation of saccharide derivatives of steroids. C. Meystre and K. Miescher (*Helv. Chim. Acta*, 1944, **27**, 231—236; cf. A., 1938, II, 174).—The yields of steroid glucosides are greatly improved if the H_2O formed by the action of the steroid and aceto-halogeno-sugar in presence of Ag_2O is removed continuously by azeotropic distillation. C_6H_6 is particularly suitable as solvent but PhMe or $CHCl_3$ can also be used. Thus are obtained: *iso*androsterone-*β*-*d*-glucoside, m.p. 216—217° and its tetra-acetate, m.p. 192°; deoxycorticosterone-*β*-*d*-glucoside, m.p. 192—195° (tetra-acetate, m.p. 172°); testosterone-*β*-α-glucoside tetra-acetate, m.p. 125—128° and 163° after re-solidification; cholesterol-*β*-*d*-glucoside; $\Delta^{5:6-20:22}$-3·21-*dihydroxynorcholadienolactone*-*β*-d-*glucoside tetra-acetate*, $[\alpha]_D^{19\cdot25}$ −34°±4° in MeOH; 3-*benzoylœstradiol*-17-*β*-*maltoside hepta-acetate*, m.p. 227—229°, $[\alpha]_D^{19\cdot5}$ +56°±4° in MeOH. Deoxycorticosterone-*β*-maltoside hepta-acetate, m.p. 183—185°, is hydrolysed to the *maltoside*, m.p. 232—235°, $[\alpha]_D^{19\cdot5}$ +124°±4° in MeOH. M.p. are corr. H. W.

III.—HOMOCYCLIC.

Dehydrogenation and decomposition of *cyclo*hexane at high temperatures over metallic catalysts. A. A. Balandin and N. Z. Kotelkov (*J. Appl. Chem. Russ.*, 1942, **15**, 139—150).—*cyclo*Hexane (**I**) was passed over heated metal spirals. There was no decomp. with Fe below 550° or with Cr-plated Fe below 500°; a little decomp. occurred with nichrome at 300°, and at higher temp. much CH_4 etc. was formed in addition to C_6H_6. Platinised nichrome dehydrogenates (**I**) at 300—400°; the rate is lowered by dilution with CO_2 at 300—350° and raised by dilution with N_2 at 400°. Soot gradually builds up on the catalyst, and the energy of activation drops from 10 kg.-cal. to 5 kg.-cal. per mol.; the activity of the catalyst has a max. at some medium soot content. An explanation is given for the promoter effect of soot. Palladised nichrome is less active than platinised nichrome, and the energy of activation (without soot) is 7 kg.-cal. J. J. B.

Photochemical nitration of benzene and nitrobenzene with nitrogen oxides.—See A., 1944, I, 109.

Vapour-phase nitration of toluene. J. L. Bullock and E. T. Mitchell (*J. Amer. Chem. Soc.*, 1943, **65**, 2426—2427).—The isomeride ratio in the gas-phase nitration of PhMe over a wide range of experimental conditions is fairly const. at 55% *o*-, 5% *m*-, and 40% *p*-$C_6H_4Me{\cdot}NO_2$. The by-products of the nitration process represent expected multiple nitration and oxidation products. W. R. A.

Polymerisation of styrene in presence of nitrothiophen and chloranil. C. C. Price (*J. Amer. Chem. Soc.*, 1943, **65**, 2380—2381).—Polymerisation of $CHPh{:}CH_2$ by Bz_2O_2 in presence of 2-nitrothiophen (**I**) or chloranil (**II**) leads to incorporation of (**I**) or (**II**), respectively, into the mol. 2-Chloroanthraquinone (**III**) is largely not so incorporated. (**I**) acts as retarder, (**II**) as a chain-transfer agent. "*Polymers*," $OBz{\cdot}[C_8H_8]_n{\cdot}C_4H_2S{\cdot}NO_2{\cdot}O_2$ (n = 10 and 16) and $Cl{\cdot}[C_8H_8]_{10}{\cdot}C_6Cl_3O_2{\cdot}O_2$, are described. (**III**) gives a product containing only 1 mol. of (**III**) per 7 mols. of polymer. R. S. C.

Chain transfer in the polymerisation of styrene. Reaction of solvents with free radicals.—See A., 1944, I, 107.

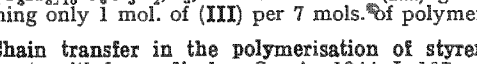
Co-polymers of *p*-chlorostyrene and methyl methacrylate. C. S. Marvel and G. L. Schertz (*J. Amer. Chem. Soc.*, 1943, **65**, 2054—2058).—Under comparable conditions, $CH_2{:}CMe{\cdot}CO_2Me$ (**I**) gives 85·6% of polymers in 45 hr., *p*-$C_6H_4Cl{\cdot}CH{:}CH_2$ (**II**) gives 23·8% in 45 hr. and 40·2% in 66 hr.; 45·2% of co-polymer is obtained from a mixture of (**I**) and (**II**) in 66 hr.; a = ratio of the rates of entry of (**II**) and (**I**) is 1·46±0·20 and is unaffected by irradiation or change of solvent. a are recorded as follows: (**I**): styrene 1·34±0·20; *m*-*chlorostyrene* (**III**): styrene 1·28±0·20; (**III**): (**I**) 1·42±0·20; (**II**): (**I**) 1·46±0·20. η of the polymer is independent of the extent of polymerisation; thus, polymerisation once started rapidly proceeds to the final stage. $CH_2{:}CH{\cdot}OAc$ and (**II**) probably do not co-polymerise. Products from (**II**) and >2 mols. of Me_2 fumarate or Et_2 maleate contain 49 mol.-% of ester. *m*-$C_6H_4Cl{\cdot}CHMe{\cdot}OH$ (prep. from *m*-$C_6H_4Cl{\cdot}MgBr$ and MeCHO), b.p. 93—94°/3 mm., with $KHSO_4$ gives (**III**), b.p. 41—43°/3 mm. R. S. C.

Homologues of *cyclo*pentyl- and *cyclo*hexyl-benzene and products of their hydrogenation. E. S. Pokrovskaja (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, **39**, 25—30).—Hydrocarbons falling into the temp. range of kerosene and Diesel oil fractions have been prepared by the action of $AlCl_3$ on a mixture of the appropriate benzenoid hydrocarbon and *cyclo*-pentene or -hexene. Some of them are reduced by H_2 at 180—190°/atm. pressure in presence of Pt–C. The following are described: cyclo*pentylmesitylene*, b.p. 276—276·5°/767 mm.; cyclo*pentyl*iso*propylbenzene*, b.p. 266·5—267·5°/757 mm.; cyclo*pentyl*-p-*cymene*, b.p. 121—122°/6·5 mm.; *di*cyclo-*pentylmesitylene*, b.p. 164—165°/1 mm.; *cyclo*hexyltoluene, b.p. 261—262°/762 mm.; *di*cyclo*hexyltoluene*, b.p. 165—166°/3 mm.; cyclo-, b.p. 237·5°/757 mm., and *di*cyclo-, b.p. 150—152°/2 mm., -*pentyltoluene*; cyclo*pentyl*-p-*xylene*, b.p. 254·5—255°/762 mm., m.p. −44°; 2-cyclo*pentyl*-1 : 3 : 5-*trimethyl*cyclo*hexane*, b.p. 254—255°/754 mm., max. NH_2Ph point 59·0°; cyclo*pentyl*-1-*methyl*-4-iso*propyl*cyclo*hexane*, b.p. 271—273°/752 mm., max. NH_2Ph point 63·7°; cyclo*hexylmethyl*cyclo*hexane*, b.p. 252—253°/756 mm., max. NH_2Ph point 55·5°. Addition of Me to hydrocarbons of the type of *cyclo*pentylbenzene has little effect on *d* or *n* but considerably increases η. Replacement of Me by Pr$^\beta$ reduces all these properties. Mono- and di-*cyclo*pentyltoluenes have higher *d* and *n* but much lower η than the corresponding *cyclo*hexyltoluenes. H. W.

Box model in theory and practice of aromatic compounds. O. Schmidt (*Ber.*, 1940, **73**, [*A*], 97—116).—A summary of work already reviewed (A., 1938, I, 298, 437; 1939, I, 183). R. S. C.

Cumulenes. III. R. Kuhn and G. Platzer (*Ber.*, 1940, **70**, [*B*], 1410—1417; cf. A., 1938, II, 354).—Compounds CRR′:C:C:C:CRR″ are readily prepared by reduction of the corresponding glycols by $CrCl_2$ when R and R′ are identical but are not obtainable if R and R′ differ either because the tendency of the electrons in the primarily formed double radicals to pass into that of the cumulenes is considerably repressed or because the reactivity of the unsymmetrical cumulenes is so greatly enhanced that they immediately react further with the HCl required for the reaction with $CrCl_2$. Successive treatments of MgEtBr in Et_2O with C_2H_2 and *p*-$OPh{\cdot}C_6H_4Bz$ lead to *aδ-diphenyl-aδ-di*-p-*phenoxyphenyl*-Δ$^\beta$-*butinene-aδ-diol*, m.p. 108°, from which the cryst. butatriene could not be obtained by means of P_2I_4 in Et_2O. aδ-Bisdiphenylene-Δ$^\beta$-butinene-aδ-diol is reduced by P_2I_4 in anhyd. Et_2O to aδ-bisdiphenylene-Δ$^{\alpha\beta\gamma}$-butatriene, m.p. 330° (vac.), softens at 320°, which does not give a colour reaction with $SbCl_3$–$CHCl_3$. With C_2H_2 and $CO(C_6H_4Me\text{-}p)_2$ MgEtBr affords *aaδδ-tetra*-p-*tolyl*-Δ$^\beta$-*butinene-aδ-diol*, m.p. 78°, converted (P_2I_4 in anhyd. Et_2O) into *aaδδ-tetra*-p-*tolyl*-Δ$^{\alpha\beta\gamma}$-*butatriene*, m.p. 240°. *aaζζ-Tetra*-p-*tolyl*-Δ$^{\beta\delta}$-*hexadi-inene-aζ-diol*, m.p. 158°, from $CO(C_6H_4Me\text{-}p)_2$, $(CH_2{:}C)_2$, and MgEtBr, is reduced [$Cr(OAc)_2$ and HCl in Et_2O] to *aaζζ-tetra*-p-*tolyl*-Δ$^{\alpha\beta\gamma\delta\varepsilon}$-*hexapentaene*, m.p. 326° (vac.), becomes black-green at 200°, and softens at 320°. Analogously, *aaζζ-tetra*-p-*chlorophenyl*-Δ$^{\beta\delta}$-*hexadi-inene-aζ-diol*, m.p. 169°, is dehydrated ($CrCl_2$) to *aaζζ-tetra*-p-*chlorophenyl*-Δ$^{\alpha\beta\gamma\delta\varepsilon}$-*hexapentaene*, m.p. 218° (vac.; decomp.). *aaζζ-Tetra*-p-*anisylhexadi-inene-aζ-diol* has m.p. 130°. Successive additions of C_2H_2 and $CPh_2{:}CO$ to MgEtBr in Et_2O give a *compound*, $C_{30}H_{22}O_2$, m.p. 187°, which is not the expected diol or diketone. Analogously a *substance*, $C_{32}H_{22}O_2$, m.p. 206—207°, results when $(CH_2{:}C)_2$ is used. $CPh_2{:}CH{\cdot}CO_2H$ is converted by $SOCl_2$ at 100° and thence by HN_3 in well cooled Et_2O into *β-phenylcinnamamide*, m.p. 130°, which is dehydrated by $SOCl_2$ to *β-phenylcinnamonitrile*, m.p. 70—71°. This when heated with $CPh_2{:}CH{\cdot}MgBr$ gives $(CPh_2{:}CH)_2$, m.p. 202°. H. W.

Polyarylated indenes. C. F. H. Allen and J. W. Gates, jun. (*J. Amer. Chem. Soc.*, 1943, **65**, 2129—2131).—The carbinol, obtained from 2 : 3 : 5 : 6-tetraphenylindenone by MgPhBr, and HBr–AcOH give 1-bromo-1 : 2 : 3 : 5 : 6-pentaphenylindene (**I**) (cf. A., 1943, II, 196). In boiling EtOH, (**I**) gives the 1-*OEt*-compound, m.p. 170—176°, and with MgPhBr–C_6H_6 gives a red solution, which in 3 days becomes colourless and then yields 1 : 1 : 2 : 3 : 5 : 6-*hexaphenylindene*, m.p. 269—270°. With Zn in AcOH, (**I**) gives 1 : 2 : 3 : 5 : 6-pentaphenylindene (**II**), m.p. 280° (cf. A., 1943, II, 37), oxidised by CrO_3–AcOH to 4 : 5 : 1 : 2-$C_6H_2Ph_2(CO_2H)_2$ (**III**) and BzOH, whereby the structure of (**II**) is proved. The hydrocarbon, m.p. 227°, obtained from 3 : 3 : 5 : 6-tetraphenylindanone (**IV**) (A., 1943, II, 67), is shown to be 1 : 1 : 3 : 5 : 6-*pentaphenylindene* by oxidation (CrO_3–AcOH) to (**III**) and BzOH. MgPhBr and (**IV**) give a glycol, which cannot be reduced to a hydrocarbon. The hydrocarbon (**V**), m.p. 222° (A., 1943, II, 37), is 1 : 1 : 2 : 5 : 6-*pentaphenylindene*; with CrO_3–AcOH it gives the *lactone*, 5 : 6-



m.p. 184—185°, converted by $NaNH_2$ in boiling *p*-cymene into 2 : 3 : 9 : 10-*tetraphenylanthracene*, m.p. 324—325°, which is also obtained from the 9 : 10-diol by KI–AcOH. The oxido-enol benzoate, m.p. (+ AcOH) 125° and (solvent-free) 196°, or ketol, m.p. 156°, from 2 : 3 : 3-triphenylindanone (Koelsch, A., 1939, II, 117), with $NaNH_2$ in *p*-cymene gives 9 : 10-diphenylanthracene. (**II**) is unaffected at 420°, but (**IV**) and (**V**) give (**II**). Dehydration of 1-hydroxy-1 : 2 : 3-triphenylindenes by acid is thus shown to involve a 1 → 3 migration of Ph. R. S. C.

***tert.*-Butyl homologues of naphthalene.** F. C. Whitmore and W. H. James (*J. Amer. Chem. Soc.*, 1943, **65**, 2088—2090).—$C_{10}H_8$, $Bu^\gamma Cl$, and $AlCl_3$ in CS_2 at 0° give $C_{10}H_7{\cdot}Bu^\gamma$ (**I**) (45%), m.p. −4°, b.p. 145°/15 mm., and mixed $C_{10}H_6Bu^\gamma_2$, m.p. 80—81°, b.p. 310—312° (cf. Bromby *et al.*, A., 1943, II, 185; Wegscheider, A., 1884, 1185). (**I**) gives a picrate, m.p. 100—101°, quinone, m.p. 76—77°, mixed liquid Br- and Cl-compounds, but not $C_{10}H_7{\cdot}CO_2H$. 1 : 2 : 3 : 4-Tetrahydronaphthalene, $Bu^\gamma Cl$, and $AlCl_3$ in CS_2 give 53% of a *tert.*-butyltetrahydronaphthalene, b.p. 100—102°/6 mm., converted by S into $C_{10}H_7Bu^\gamma$ (50%), b.p. 106—107°/5 mm. $C_{10}H_8$, $CMe_2{:}CH_2$, and $AlCl_3$ in CS_2 give 34% of $C_{10}H_7Bu^\gamma$, b.p. 278°/735 mm., 144—146°/15 mm., and a large amount of viscous oil. R. S. C.

Diterpenes. Synthesis of 3 : 6-dimethyl-1-*iso*propylacenaphthene and of 1 : 5-dimethyl-2-naphthol. L. Ruzicka and E. Rey (*Helv. Chim. Acta*, 1943, **26**, 2136—2142).—*p*-$C_6H_4Me{\cdot}COPr^\beta$ is converted

by $CH_2Cl{\cdot}CO_2Et$ and Mg activated by I in abs. Et_2O into *Et β-hydroxy-β-p-tolyl-γ-methyl-n-valerate*, b.p. ~150°/13 mm., transformed by successive treatments with PBr_3 in cold C_6H_6 and $NPhMe_2$ at 230° into *Et β-p-tolyl-γ-methyl-Δ$^{\alpha}$-pentenoate* b.p. 104—108°/0·4 mm. (corresponding *acid*, b.p. 110°/0·1 mm.). This is hydrogenated (Pt in AcOH) to *Et β-p-tolyl-γ-methylvalerate*, b.p. 92°/0·3 mm., hydrolysed to the *acid* (**I**), m.p. 77. (**I**) is transformed by $SOCl_2$ into the corresponding chloride, b.p. 113°/1 mm., converted by $AlCl_3$ in CS_2 into 1-*keto*-6-*methyl*-3-iso*propylindane*, b.p. 148—155°/10 mm. [*semicarbazone*, m.p. 194° (decomp.)], which with activated Mg and $CHMeBr{\cdot}CO_2Et$ in Et_2O affords *Et α-1-hydroxy-6-methyl*-3-iso*propyl*-1-*indanylpropionate*, b.p. 173—178°/11 mm. This is converted by successive treatments with PBr_3 and $NPhMe_2$ into *Et α-6-methyl*-3-iso*propyl*-1-*indanylidenepropionate*, b.p. 129—130°/0·8 mm., reduced (Bouveault) to *β-6-methyl*-3-iso*propyl*-1-*indanyl-propyl alcohol*, b.p. 122—124°/0·1 mm. The corresponding *bromide*, b.p. 129—130°/0·2 mm., is converted by KCN in EtOH at 100° followed by hydrolysis into *β-6-methyl*-3-iso*propyl*-1-*indanyl*-n-*butyric acid*, b.p. 170°/6 mm. cyclised by successive treatments with $SOCl_2$ and $AlCl_3$ in CS_2 at room temp. to 6-*keto*-3 : 6-*dimethyl*-1-iso*propyltetrahydroacenaphthene* (**II**), b.p. 145°/0·5 mm. (*semicarbazones*, m.p. 204—205° and 167—168° respectively). This is reduced (Na and EtOH) to the corresponding carbinol, b.p. 134°/0·5 mm., which is dehydrogenated (Se at 350°) to 3 : 6-*dimethyl*-1-iso*propyl-acenaphthene*, b.p. 125°/0·05 mm. (*picrate*, m.p. 109—110; *styphnate*, m.p. 120—121°; additive *compound*, m.p. 93·5—94·5°, with *s*-$C_6H_3(NO_2)_3$], not identical with the hydrocarbon $C_{17}H_{20}$ obtained by the dehydrogenation of agathicdicarboxylic acid (A., 1931, 231).

1 : 5-Dimethyl-3 : 4-dihydronaphthalene is converted by *o*-$CO_2H{\cdot}C_6H_4{\cdot}CO_3H$ in Et_2O into 2-*keto*-1 : 5-*dimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b.p. 160—163°/13 mm., transformed by Pd-C at 300—325° into 1 : 5-*dimethyl*-2-*naphthol*, m.p. 158—159°. 5-Keto-2-methoxy-1-methyl-5 : 6 : 7 : 8-tetrahydronaphthalene is converted by successive treatments with MgMeI and I at 150° into 2-methoxy-1 : 5-dimethyl-7 : 8-dihydronaphthalene, which is dehydrogenated by Se at 330° to 2-*methoxy*-1 : 5-*dimethylnaphthalene*, m.p. 92—93° (*picrate*, m.p. 91—92°). M.p. are corr. H. W.

Sesquiterpenes. LXII. Novel sesquiterpene hydrocarbon from the leaf oil of *Cedrus atlantica*, Manetti. L. Ruzicka, H. Schinz, and P. H. Müller (*Helv. Chim. Acta*, 1944, **27**, 195—206).—A fraction of the oil, b.p. 90—104°/0·3 mm., dissolved in dry Et_2O is converted by HCl at 0° into the *sesquiterpene dihydrochloride* (**I**), m.p. 117—118°, $[\alpha]_D$ −7·90° in $CHCl_3$, converted by boiling MeOH or, less advantageously, by heating at 120—150° into the *monohydrochloride*, m.p. 59—60°, $[\alpha]_D^{15}$ +104° in $CHCl_3$, from which (**I**) is regenerated by HCl in Et_2O. (**I**) and boiling 20% KOH–MeOH slowly yield the *hydrocarbon*, $C_{15}H_{24}$ (**II**), b.p. 128—129°/12 mm., $[\alpha]_D$ +67·2°. Ozonisation of (**II**), with or without after-oxidation by $KMnO_4$, does not afford large homogeneous fragments, CH_2O, or $COMe_2$ so that the double linkings appear to be within the ring and :CH_2 or :CMe_2 is not present. At 310° (**II**) is dehydrogenated by Se mainly to 1 : 6-$C_{10}H_6Me_2$. Dehydrogenation, best with Pd containing 1% of Cu at 310°, gives also a *hydrocarbon*, $C_{15}H_{18}$, m.p. 81—82°, characterised by its *picrate*, m.p. 165—166°, and additive *compound*, m.p. 191°, with *s*-$C_6H_3(NO_2)_3$, and apparently, according to its absorption spectrum, closely related to the polyalkylnaphthalenes. *p*-$C_6H_4Me{\cdot}CH_2{\cdot}CHO$, activated Zn filings, and $CHPr^{\beta}Br{\cdot}CO_2Et$ in abs. C_6H_6 afford *Et β-hydroxy-γ-p-tolyl-α-isopropylvalerate*, b.p. 130—131°/0·05 mm., converted by PBr_3 and C_5H_5N in anhyd. Et_2O followed by vac.-distillation into *Et γ-p-tolyl-α-isopropyl-Δ$^{\alpha}$-pentenoate*, b.p. 115—117°/0·05 mm., which is reduced (Raney Ni and 96% EtOH) and then hydrolysed to *γ-p-tolyl-α-isopropyl-n-valeric acid*, b.p. 113—118°/0·04 mm. This is cyclised by successive treatments with $SOCl_2$ in boiling Et_2O and $AlCl_3$ in CS_2 to 4-*keto*-1 : 6-*dimethyl*-3-iso*propyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b.p. 98—102°/0·05 mm., which is reduced by Na and EtOH and then dehydrated and dehydrogenated (S) to 1 : 6-*dimethyl*-3-iso*propylnaphthalene*, b.p. 148°/10 mm. [*picrate*, m.p. 107—108°; *styphnate*, m.p. 127—128°; additive *compound*, m.p. 115—116°, with *s*-$C_6H_3(NO_2)_3$].

[With A. Senensieb and S. I. van Welie.] Pure *p*-xylene is transformed into 4-keto-1 : 2 : 5 : 8-tetramethyl-1 : 2 : 3 : 4-tetrahydronaphthalene (**III**) (cf. A., 1933, 494), which is reduced to the carbinol and then dehydrated and dehydrogenated by S at 180—230° (instead of Se) to 1 : 2 : 5 : 8-tetramethylnaphthalene, b.p. 167—172°/13 mm. [picrate, m.p. 146—147°; additive compound, m.p. 166—167°, with *s*-$C_6H_3(NO_2)_3$]. (**III**) is treated with an excess MgMeI in boiling Et_2O, any unchanged ketone is removed by Girard's reagent *T*, and the carbinol is transformed by S at 220° into 1 : 2 : 4 : 5 : 8-$C_{10}H_3Me_5$, b.p. 110°/0·04 mm., m.p. 60—61° [picrate, m.p. 156—157°; additive *compound*, m.p. 179—180°, with *s*-$C_6H_3(NO_2)_3$].

[With K. Jirasek and O. R. Riklin.] Homogeneous *m*-xylene is transformed into 4-keto-1 : 2 : 6 : 8-tetramethyl-1 : 2 : 3 : 4-tetrahydronaphthalene (**IV**), b.p. 107—108°/0·07 mm. (semicarbazone, m.p. 217°), which is reduced to the carbinol, converted by S at 230° into 1 : 2 : 6 : 8-$C_{10}H_4Me_4$, b.p. ~100°/0·02 mm. [*picrate*, m.p. 133—134°; additive *compound*, m.p. 153—154°, with *s*-$C_6H_3(NO_2)_3$; styphnate, m.p. 148—150°]. (**IV**) is treated with an excess of MgMeI followed by Girard's reagent *T* and the carbinol is heated with I at 160°, whereby disproportionation occurs to 1 : 2 : 4 : 6 : 8-*pentamethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (**V**), b.p. 136°/13 mm., and 1 : 2 : 4 : 6 : 8-$C_{10}H_3Me_5$, b.p. 173—178°/10 mm., m.p. 101—102° [picrate, m.p. 171—172°; additive *compound*, m.p. 183—184°, with *s*-$C_6H_3(NO_2)_3$], also obtained by heating (**V**) with S at 220°. H. W.

Benz*cyclo*octatetraenes. IV. 1 : 2 : 3 : 4 : 5 : 6-tribenz-Δ$^{1:3:5:7}$-*cyclo*octatetraene. R. G. Shuttleworth and (in part) W. S. Rapson and E. T. Stewart. **V. Absorption spectra of tetraphenylene and 1 : 2 : 3 : 4 : 5 : 6-tribenz-Δ$^{1:3:5:7}$-*cyclo*octatetraene in relation to their structures.** W. S. Rapson, (Miss) H. M. Schwartz, and E. T. Stewart (*J.C.S.*, 1944, 71—73, 73—74; cf. A., 1933, II, 197).—IV. Tetraphenylene (**I**) on oxidation (CrO_3) gives 1 : 2 : 3 : 4 : 5 : 6-*tribenz*cyclo*octatetraene*-7 : 8-*dicarboxylic anhydride* (**II**), m.p. 228—229°, which on decarboxylation gives 1 : 2 : 3 : 4 : 5 : 6-*tribenz*-Δ$^{1:3:5:7}$-cyclo*octatetraene* (**III**), m.p. 138·5—139°, stable to $KMnO_4$ and giving no picrate. (**III**) gives 1 : 2 : 3 : 4 : 5 : 6-*tribenz*-Δ$^{1:3:5:7}$-cyclo*octatetraene* 7 : 8-*dibromide*, m.p. 155—156°, and is reduced (Pt catalyst) to 1 : 2 : 3 : 4 : 5 : 6-tribenz-Δ$^{1:3:5}$-*cyclo*octatriene, m.p. 111—113°. Further oxidation (CrO_3) of (**II**) gives *o-diphenylbenzene-2′ : 2′′-dicarboxylic acid* (**IV**), m.p. 262·5—263·4°, identical with a specimen prepared by the Ullmann reaction from Et 2-iododiphenyl-2′-carboxylate and *o*-$C_6H_4I{\cdot}CO_2Et$. Identification of (**IV**) establishes the structures of (**I**) and (**III**).

V. A close similarity is found between the absorption spectra of tetraphenylene and 2 : 2′-diphenyldiphenyl, suggesting a non-planar structure for tetraphenylene, a hypothesis supported by *X*-ray crystallographic analysis. The absorption spectrum of 1 : 2 : 3 : 4 : 5 : 6-tribenz-Δ$^{1:3:5:7}$-*cyclo*octatetraene also shows none of the attributes of a compound containing condensed aromatic rings. These results support the view that *cyclo*octatetraene itself is non-planar and non-aromatic in type. D. G.

Polycyclic systems. II. Naphtha-2′ : 3′-1 : 2-chrysene, a new hydrocarbon of the 1 : 2-benzanthracene series. M. Beyer and J. Richter (*Ber.*, 1940, **73**, [*B*], 1319—1328; cf. A., 1938, II, 236).—Chrysene and *o*-$C_6H_4(CO)_2O$ in C_6H_6 containing $AlCl_3$ at 35—45° give o-2-*chrysenoylbenzoic acid* (**I**), m.p. 213—214° (*Me*, m.p. 176—177°, and *Et*, m.p. 134°, ester), which gives a red-brown solution in conc. H_2SO_4, rapidly becoming violet and then bright blue, and a blue colour which rapidly becomes brown-red with $SbCl_5$ in $CHCl_3$. It is transformed by PCl_5 in C_6H_6 into the *chloride*, m.p. 219°, which reacts very slowly with alcohols, is moderately stable towards H_2O, but is rapidly converted by aq. NH_3 into o-2-*chrysenoylbenzamide*, m.p. 158° (decomp.), becomes yellow at 138° and softens at 148°. (**I**) is reduced by Zn–Hg and HCl in boiling AcOH to o-2-*chrysenylmethylbenzoic acid*, m.p. 246—247° (*Na* salt; *Me*, m.p. 150—151°, and *Et*, m.p. 174° ester). (**I**) and BzCl in 1-$C_{10}H_7Cl$ at 245—255° afford *naphtha-2′ : 3′-1 : 2-chrysene*-1 : 4′-*quinone* (**II**), m.p. 272°, hydrogenated (PtO_2 in AcOH) to a non-cryst. H_6-derivative. (**II**) could not be caused to react with $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2,HCl$, MgMeI, or P + HI but is converted by yellow P in boiling $EtCO_2H$ containing a little I into 4′-*propionoxynaphtha-2′ : 3′-1 : 2-chrysene* (**III**), m.p. 200—201°, transformed by NaOH and Devarda's alloy in boiling aq. EtOH into (**II**). Distillation of (**III**) with electrolytic Zn dust affords 1′-*keto*-1′ : -*dihydronaphtha-2′ : 3′-1 : 2-chrysene*, m.p. 285—286°, also obtained from (**III**), NaCl, somewhat moist $ZnCl_2$, and Zn dust at 280°; it does not react with $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2,HCl$, NH_2OH,HCl, MgMeI in Et_2O, Bu^{α}_2O, or PhEt or with P + I. (**II**) is reduced by Zn–Hg and 12N-HCl in boiling AcOH–PhMe under H_2 followed by chromatography over Al_2O_3 into *naphtha-2′ : 3′-1 : 2-chrysene*, m.p. 185—186°, in small yield. It gives a cryst additive *product*, m.p. 169°, with *s*-$C_6H_3(NO_2)_3$, and adducts of indefinite m.p. with picric acid, styphnic acid, 2 : 7-dinitroanthraquinone, and erythritol tetranitrate. During its prep. it appears to give an additive *product*, $C_{28}H_{16},C_{26}H_{16}$, which does not give adducts with picric acid or 2 : 7-dinitroanthraquinone. H. W.

"Oxidising" actions of alkalis. VI. *o*-Nitrotoluene. G. Luck [with F. Stitz] (*Ber.*, 1940, **73**, [*B*], 1377—1381).—Treatment of *o*-$C_6H_4Me{\cdot}NO_2$ with 70% KOH at 200° gives *o*-toluidine (**I**) and *o*-$NH_2{\cdot}C_6H_4{\cdot}CO_2H$ (**II**) in preparative yields of 18·2% and 15·7% respectively, with some 2 : 2′-azoxytoluene, m.p. 58·5°. The mechanism is probably: $C_6H_4Me{\cdot}NO_2 + 3KOH \rightarrow 3H_2O +$ $NO_2{\cdot}C_6H_4{\cdot}C(OK)_3$; $NO_2{\cdot}C_6H_4{\cdot}CO_2K + 3H_2 \rightarrow NH_2{\cdot}C_6H_4{\cdot}CO_2K + 2H_2O$; $C_6H_4Me{\cdot}NO_2 + 3H_2 \rightarrow$ (**I**) $+ 2H_2O$; $2C_6H_4Me{\cdot}NO_2 + 3H_2 \rightarrow C_6H_4Me{\cdot}NO{:}N{\cdot}C_6H_4Me + 3H_2O$. 1 : 4 : 2- and 1 : 3 : 2-$C_6H_3Me_2{\cdot}NO_2$ give small amounts of NH_3 and HCN, small amounts of the corresponding amines, but no homogeneous NH_2-acid. *o*-$C_6H_4Et{\cdot}NO_2$ yields NH_3, HCN, unchanged product, *o*-$C_6H_4Et{\cdot}NH_2$ and resin. (**I**) and (**II**) are almost quantitatively recovered. Anthranil affords a little NH_3 and HCN, (**II**), and resin. *o*-$NO_2{\cdot}C_6H_4{\cdot}CO_2H$ reacts very vigorously, giving very little NH_3 and being mainly resinified. $PhNO_2$ is largely unchanged but gives a little NH_3, $(NPh)_2$, and resin. H. W.

Identification of alkylbenzenes. III. Acetamido- and benzamido-derivatives of *iso*butylbenzene. V. N. Ipatiev and L. Schmerling (*J. Amer. Chem. Soc.*, 1943, **65**, 2470; cf. A., 1938, II, 316).—PhBu$^{\beta}$, b.p. 166—170° [NHAc-, m.p. 127—128°, (*NHAc*)$_2$-, m.p. 210—211°, and *NHBz*-derivative, m.p. 128—129°], is prepared in 30 and 10% yield, respectively, from (i) PhBr, Bu$^{\beta}$Br, and Na in C_6H_6 or (ii) $CH_2Ph{\cdot}MgCl$ and Pr$^{\beta}$Br in Et_2O. R. S. C.

***dl*-β-Phenyl-*n*-propylmethylamine, b.p. 211° (hydrochloride, m.p. 144°).**—See A., 1944, III, 279.

β-Anilinobutadienes.—See B., 1944, II, 100.

Derivatives of acetanilide. L. S. Fosdick and G. W. Rapp (*J. Amer. Chem. Soc.*, 1943, **65**, 2307—2308).—$CH_2Cl{\cdot}COCl$ with NH_2Ph or $NO_2{\cdot}C_6H_4{\cdot}NH_2$ in $COMe_2$ gives $NHPh{\cdot}CO{\cdot}CH_2Cl$ or $NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}CH_2Cl$, respectively, converted by NHR_2 in hot $COMe_2$ into $NHPh{\cdot}CO{\cdot}CH_2{\cdot}NR_2$ or $NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}NR_2$ (*A*), respectively. H_2–PtO_2 in EtOH at 40—50 lb. reduces (*A*) to $NH_2{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}NR_2$ (*B*). The following (m.p. in parentheses are those of *hydrochlorides* or, for diamines, *dihydrochlorides*) are thus prepared: *ω-dipropyl-*, b.p. 145—146°/1·5 mm. (m.p. 184—186°), and *ω-dibutyl-aminoacetanilide*, b.p. 155—156°/1 mm. (m.p. 101—102°); m- (m.p. 195—197°) and p-*nitro-ω-diethylaminoacetanilide*, m.p. 44—46°; o-, m.p. 48·5—50° (m.p. 114—115°), m- (m.p. 147—149°), and p-*nitro-ω-dipropylaminoacetanilide*, m.p. 46—48°; o- (m.p. 132—133°), m- (m.p. 131—132°), and p-*nitro-ω-dibutylaminoacetanilide*, m.p. 75—76°; *m-* (m.p. 231—234°), and p-*amino-ω-diethylaminoacetanilide* (m.p. 235—240°); *o-* (m.p. 182—183°), *m-* (m.p. 180—182°), and *p*-amino-ω-dipropylaminoacetanilide (m.p. 269—273°); o- (m.p. 178—180°), m- (m.p. 172—174°), and p-*amino-ω-dibutylaminoacetanilide*, m.p. 43—45°. (*B*) have slight anæsthetic activity; substitution by NH_2 and increase in mol. wt. decrease the action; NO_2 destroys it. (*A*) have slight vasopressor activity. (*A*) and (*B*) are highly toxic. R. S. C.

β-Nitrosoacylarylamides.—See A., 1944, II, 120.

Monoreduction of 1 : 3-dinitronaphthalene and separation of 3-nitro-1- and 4-nitro-2-naphthylamine. H. H. Hodgson and S. Birtwell (*J.C.S.*, 1944, 75—77).—1 : 3-$C_{10}H_6(NO_2)_2$ (**I**) and aq. Na_2S–$NaHCO_3$–MeOH (boil for 20 min.) afford 87% of 3 : 1-$NO_2{\cdot}C_{10}H_6{\cdot}NH_2$ (**II**) (mainly) (Ac derivative, new m.p. 259°) and 4 : 2-$NO_2{\cdot}C_{10}H_6{\cdot}NH_2$ (**III**) (Ac derivative, new m.p. 241°). Mixtures of (**II**) and (**III**) are separable by preferential acetylation [of (**III**)] with Ac_2O in AcOH–NaOAc. (**II**) or (**III**) with boiling 90% HCO_2H gives 3-*nitroform*-1-, m.p. 216°, or 4-*nitroform*-2-*naphthalide*, m.p. 205°, respectively. (**I**) and H_2S–C_5H_5N give 75% of mixed (**II**) + (**III**). 3 : 1-$NO_2{\cdot}C_{10}H_6{\cdot}N_2Cl$ is stable; its $ZnCl_2$ double salt and boiling EtOH give 2-$C_{10}H_7{\cdot}NO_2$ whilst the Sandmeyer reaction affords 1 : 3-$C_{10}H_6Cl{\cdot}NO_2$, new m.p. 129·5°, and 2-*nitro*-4-*cyanonaphthalene*, m.p. 163°. A. T. P.

Relation between chemical structure and bacteriostatic activity of sulphanilamide-type compounds.—See A., 1944, III, 294.

Acetylsulphanilylguanidine. A. Divinski and S. Vorobieva (*Compt. rend. Acad. Sci. U.R.S.S.*, 1942, **36**, 203—205).—Acetylsulphanilylguanidine (**I**), m.p. 263—264°, is obtained in 50% yield by the gradual addition of *p*-NHAc·$C_6H_4{\cdot}SO_2Cl$ to a mixture of 50% NaOH, $NH{:}C(NH_2)_2{,}HNO_3$, and C_5H_5N bases at 10—15°. It is quantitatively deacetylated at 100° by 10% HCl to sulphanilylguanidine. In Marshall's method (A., 1941, III, 786) (**I**) is accompanied by a small proportion of a compound, m.p. 290°. Contrary to Marshall the solubility of (**I**) in H_2O is 2·5% (see also A., 1944, III, 358). H. W.

Synthesis of di-β-naphthylthiocarbazone and its analogues. D. M. Hubbard and E. W. Scott (*J. Amer. Chem. Soc.*, 1943, **65**, 2390—2393).—β-$C_{10}H_7{\cdot}N_2Cl$–HCl–NaOAc–H_2O and $MeNO_2$–NaOH–H_2O–EtOH at 0° give (β-$C_{10}H_7{\cdot}N_2)_2CH{\cdot}NO_2$, m.p. 198—200°, converted by NH_3–H_2S–EtOH at 0° into unstable β-$C_{10}H_7{\cdot}NH{\cdot}N{:}C(SH){\cdot}NH{\cdot}NH{\cdot}C_{10}H_7$-β, m.p. 135—137° (decomp.), which with 5% KOH–EtOH gives β-$C_{10}H_7{\cdot}NH{\cdot}N{:}C(SH){\cdot}N{:}N{\cdot}C_{10}H_7$-β (purified by treatment in warm $CHCl_3$ with NH_2OH), β-$C_{10}H_7{\cdot}NH{\cdot}NH{\cdot}CS{\cdot}NH_2$, and $C_{10}H_7{\cdot}NH_2$. Similarly are prepared $(ArN_2)_2CH{\cdot}NO_2$ in which Ar = Ph, m.p. 150—152°, *o-*, m.p. 153—154°, and *p*-tolyl, m.p. 160—162°, *p*-C_6H_4Ph, m.p. 168—170°, α-$C_{10}H_7$, m.p. 160—162°, *p*-$NH_2{\cdot}SO_2{\cdot}C_6H_4$, m.p. 208—210°, *p*-$C_6H_4Br$, m.p. 156—158°, and *p*-$NO_2{\cdot}C_6H_4$·, m.p. 138—140°, NHAr·N:C(SH)·NH·NHAr in which Ar = Ph, m.p. 156—158° (decomp.), *o-*, m.p. 140—142° (decomp.), and *p*-tolyl, m.p. 145—147° (decomp.), *p*-C_6H_4Ph, m.p. 215—217° (decomp.), and *p*-C_6H_4Br, m.p. 125° (decomp.), and NHAr·N:C(SH)·N:NAr (*A*) in which Ar = Ph, *o-* and *p*-tolyl, *p*-C_6H_4Ph, α-$C_{10}H_7$, and *p*-C_6H_4Br. Transmittancy curves of five (*A*) and four derived Hg complexes in $CHCl_3$ are recorded. R. S. C.

Kinetics of formaldehyde–phenol condensation.—See A., 1944, I, 106.

Effect of changes in the acyl group on the Fries reaction with esters of 2 : 6-dichlorophenol and 2 : 6-dimethylphenol. D. S. Tarbell and P. E. Fanta (*J. Amer. Chem. Soc.*, 1943, **65**, 2169—2174).—Fries rearrangement of 2 : 6 : 1-$C_6H_3R_2{\cdot}OAcyl$ (R = Cl or Me) is hindered if $C_{(\alpha)}$ of the acyl is substituted by Me, Cl, or Ph. The rearrangement is held to be probably a bimol. acylation. Esters described below were prepared from 2 : 6 : 1-$C_6H_3Cl_2{\cdot}OH$ (**I**) and RCOCl in C_5H_5N except for the chloroacetates which are obtained from the K phenoxide (**II**) and acyl chloride. (**II**) and $CH_2Cl{\cdot}COCl$ in boiling Et_2O give 2 : 6 : 1-$C_6H_3Cl_2$ *chloroacetate* (**III**) (61%), b.p. 115—116°/2 mm., and 2 : 6-*dichlorophenoxyacetate* (**IV**) (5%), m.p. 153—153·5°. Hydrolysis of (**IV**) gives 2 : 6-*dichlorophenoxyacetic acid*, m.p. 134·5—135°, also obtained from (**I**) and $CH_2Cl{\cdot}CO_2H$. Conditions described below are the optimum for prep. of the OH-ketone, 1·1 mol. of $AlCl_3$ and no solvent being used in each case. 2 : 6 : 1-$C_6H_3Cl_2$ *propionate*, b.p. 113—115°/0·5 mm., at 135—145° (2 hr.) gives 3 : 5-*dichloro*-4-*hydroxypropiophenone* (87%), m.p. 110—111°, and 7% of (**I**); with BF_3 it gives a solid complex, unstable at 100°, but decomp. thereof at 200° gives no ketone. 2 : 6 : 1-$C_6H_3Cl_2$ iso*butyrate*, b.p. 130—130·5°/3 mm., at 130—135° (4·5 hr.) gives 3 : 5-*dichloro*-4-*hydroxy*iso*butyrophenone* (42%), m.p. 112—113°, with 46% (? 32%) of phenol [little (**I**)]. 2 : 6 : 1-$C_6H_3Cl_2$ αα-*dimethylpropionate* (**V**), b.p. 130—132°/3 mm., at 120° (0·25 hr.) gives 71% of (**I**) and no ketone, and at 155° (1 hr.) gives only tars. 2 : 6 : 1-$C_6H_3Cl_2$ ββ-*dimethyl*-n-*butyrate*, b.p. 114—116°/1 mm., at 135—145° (2 hr.) gives 3 : 5-*dichloro*-4-*hydroxy*-ββ-*dimethyl*-n-*butyrophenone* (28%), m.p. 94—95·5°, and 5% of (**I**). At 112—114° (2·5 hr.) (**III**) gives 3 : 5 : α-*trichloro*-4-*hydroxyacetophenone* (77%), m.p. 120—121° [2 : 4-*dinitrophenylhydrazone*, m.p. 221—223° (decomp.); with NaOI gives 4 : 3 : 5 : 1-OH·$C_6H_2Cl_2{\cdot}CO_2H$], and 2% of (**I**). 2 : 6 : 1-$C_6H_3Cl_2$ *dichloroacetate*, b.p. 113—114°/0·5 mm., at 134° (2 hr.) gives 3 : 5 : αα-*tetrachloro*-4-*hydroxyacetophenone* (9%), m.p. 92·5—94·5° [with *p*-$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}NH_2$ gives 3 : 5-*dichloro*-4-*hydroxyphenylglyoxal*-p-*nitrophenylosazone*, m.p. 289·5—290° (hot stage)], and 79% of unchanged ester. 2 : 6 : 1-$C_6H_3Cl_2$ *trichloroacetate*, b.p. 119—120°/1 mm., is largely unchanged at 110° (5 hr.) and at 137° gives tars. 2 : 6 : 1-$C_6H_3Cl_2$ *phenylacetate*, b.p. 167—172°/2 mm., at 112° (4 hr.) gives 4 : 3 : 5 : 1-OH·$C_6H_2Cl_2$ CH_2Ph *ketone* (26%), m.p. 136·5—138° (p-*nitrophenylhydrazone*, m.p. 227·5—228·5°), and 28% of unchanged ester, but only tars could be obtained from 2 : 6 : 1-$C_6H_3Cl_2$ *diphenylacetate*, m.p. 132—133°. 2 : 6 : 1-$C_6H_3Cl_2$ *benzoate*, m.p. 74—74·5°, at 154° (2·5 hr.) gives 3 : 5-*dichloro*-4-*hydroxybenzophenone* (71%), m.p. 145—146°, with 10% each of (**I**) and unchanged ester; the *mesitoate*, m.p. 84·5—85·5°, at 155° (1 hr.) gives 3 : 5-*dichloro*-4-*hydroxy*-2′ : 4′ : 6′-*trimethylbenzophenone* (79%), m.p. 201·5—203°. m-2-*Xylyl* iso*butyrate*, b.p. 126—128°/22 mm., at 125° (3·5 hr.) gives 94% of 4-*hydroxy*-3 : 5-*dimethyl*iso*butyrophenone*, m.p. 106·5—107°, but the αα-*dimethylpropionate*, b.p. 80—83°/0·5 mm., and *trichloroacetate*, m.p. 58·5—59·5°, are unchanged or yield tars. With $AlCl_3$ in $PhNO_2$ at room temp. (48 hr.) 2 : 6 : 1-$C_6H_3Cl_2{\cdot}O{\cdot}COPr^{\alpha}$ gives 20% of (**I**) (the amount varying with the quality of the $AlCl_3$) (cf. A., 1943, II, 283); similar treatment of (**V**) gives 40% of (**I**). Ph_2O, (**V**), and $AlCl_3$ in boiling CS_2 give 73% of (**I**) and a small amount of impure p-*phenoxy*-αα-*dimethylpropiophenone*, obtained pure [m.p. 52—52·5° (2 : 4-*dinitrophenylhydrazone*, m.p. 172—173°)] by the direct Friedel–Crafts reaction. M.p. are corr. R. S. C.

Synthesis of 3 : 6-dimethyl-1-*iso*propylacenaphthene and of 1 : 5-dimethyl-2-naphthol.—See A., 1944, II, 124.

Syntheses in the naphthalene series. III. 1-Hydroxy-2 : 3-benzfluorene and 4-hydroxy-2-methyl-5 : 6-benzcoumaran. A. Latif and G. Soliman (*J.C.S.*, 1944, 56—58).—$CH_2Ph{\cdot}CO{\cdot}CHNa{\cdot}CO_2Et$ and CH_2PhCl yield *Et* γ-*phenyl*-α-*benzylacetoacetate*, b.p. 182—184°/7 mm., converted by cold H_2SO_4 into 1-*hydroxy*-2 : 3-*benzfluorene*, m.p. 164° (*acetate*, m.p. 171°; *Me ether*, m.p. 70°) [Zn dust distillation gives 2 : 3-benzfluorene (**I**)]. Similarly, *Et* γ-*phenyl*-α-*allylacetoacetate*, b.p. 160—162°/6 mm., gives 4-*hydroxy*-2-*methyl*-5 : 6-*benzcoumaran*, m.p. 130° (*monoacetate*, m.p. 93°), oxidised by CrO_3–AcOH to 2-methyl-5 : 6-benzcoumaran-4 : 7-quinone, m.p. 167°. $CH_2Ph{\cdot}CHAc{\cdot}CO_2Et$ and cold H_2SO_4 give a low yield of 3-methylindene-2-carboxylic acid, m.p. 199—200°. *o*-$C_6H_4(CHO)_2$ and α-hydrindone in MeOH–KOH give 2 : 3-benzfluorenone and thence (Zn dust) (**I**). A. T. P.

Synthetic œstrogenic compounds related to stilbene and diphenylethane. II. E. C. Dodds, L. Golberg, E. I. Grünfeld, W. Lawson, C. M. Saffer, jun., and (Sir) R. Robinson (*Proc. Roy. Soc.*, 1944, **B**, **132**, 83—101; see also, A., 1944, III, 343).—αβ-*Dianisylpropan*-β-*ol*, m.p. 62—63° [from deoxyanisoin (**I**) and Et_2O–MgMeI], is dehydrated ($KHSO_4$ at 190°) to 4 : 4′-*dimethoxy*-α-*methylstilbene*, m.p. 123—124°, demethylated (EtOH–KOH at 190°; general procedure unless stated otherwise) to the 4 : 4′-(*OH*)$_2$-derivative, m.p. 181—182° (diacetate, m.p. 124—125°; dibenzoate, m.p. 176—177°). MgBu^{a}Cl and (**I**) give (*p*-$OMe{\cdot}C_6H_4{\cdot}CH{:}$)$_2$ and the *Me*$_2$ *ether*, b.p. 190—195°/0·4 mm., of 4 : 4′-*dihydroxy*-α-n-*butylstilbene*, m.p. 114°. Similarly prepared are 4 : 4′-*dimethoxy*-α-iso*butyl*-, b.p. 164—168°/0·05 mm., -α-n-*propyl*-, b.p. 183—185°/0·07 mm., -α-iso*propyl*-, b.p. 172—176°/0·4 mm., -α-n-*amyl*-, b.p. 195—198°/0·1 mm., and -α-cyclo*hexyl*-, b.p. 190°/0·05 mm., and 4 : 4′-*dihydroxy*-α-iso*butyl*-, m.p. 128°, -α-n-*propyl*-, m.p. 91°, -α-iso*propyl*-, m.p. 166°, -α-n-*amyl*-, m.p. 96°, and -α-cyclo*hexyl*-*stilbene*, m.p. 136°. Reduction [H_2 (1 atm.), Pd–C, $COMe_2$, room temp.] of *cis*- (**II**) or *trans*-(*p*-$OMe{\cdot}C_6H_4{\cdot}CEt{:}$)$_2$ (**III**) affords the same H_2-derivative (**IV**), m.p.

145—146°, but similar reduction at 45° of a mixture of (**II**) and (**III**) gives (**IV**) and a little of an isomeric H_2-derivative (**V**), b.p. 161—163°/0·09 mm., m.p. 56—57°. Similar reduction of ψ-diethylstilbœstrol (impure; m.p. 140—142°) affords *meso*-(*p*-OH·C_6H_4·CHEt)$_2$ (hexœstrol) (**VI**), m.p. 184—185°; a little diethylstilbœstrol (**VII**) (? originally present) is also isolable. (**VII**) is hydrogenated to *dl*-(*p*-OH·C_6H_4·CHEt)$_2$, m.p. 128° [Me_2 *ether* (prep. by Me_2SO_4), m.p. 56—57°, = (**V**)]. γδ-Dianisylhexane, m.p. 145—146°, is demethylated [AcOH–HI (*d* 1·7) at 150°] to (**VI**). Reduction of (*p*-OMe·C_6H_4·CMe:)$_2$ gives βγ-*dianisyl*-n-*butane*, m.p. 87—88°, demethylated (AcOH–HI at 160—170°) to the (*OH*)$_2$-derivative, m.p. 138—139°. Methyldeoxyanisoin (**VIII**), Mg, and CH_2:CH·CH_2Br in Et_2O afford 4 : 4′-*dimethoxy*-α-*methyl*-β-*allylstilbene*, b.p. 188—192°/0·25 mm., m.p. 103°, whence 4 : 4′-*dihydroxy*-α-*methyl*-β-*allyl*- (or -*propenyl*-)*stilbene*, m.p. 162°. The product from (**VIII**) and MgPr^{n}Br is dehydrated ($KHSO_4$ at 180—190°) to 4 : 4′-*dimethoxy*-α-*methyl*-β-n-*propylstilbene*, b.p. 178—180°/0·09 mm., demethylated to mixed (*OH*)$_2$-derivatives, b.p. 201—202°/0·23 mm. [*dibenzoates*, m.p. 140—141° and 202—204° (**IX**)]; hydrolysis (aq. MeOH–KOH) of (**IX**) gives the trans-(*OH*)$_2$-compound, m.p. 158°. Catalytic reduction of (*p*-OMe·C_6H_4·CPr^a:)$_2$ affords δε-*dianisyloctane*-a, m.p. 121—122°, and -b, b.p. 175—177°/0·06 mm., demethylated (AcOH–HI) to δε-*di*-p-*hydroxyphenyloctane*-a, m.p. 165° (poor yield), and -b, b.p. 185—187°/0·1 mm., respectively. n-$C_{16}H_{33}Br$ added to (**I**) in EtOH–NaOEt gives *cetyldeoxyanisoin* (**X**), b.p. 262—265°/0·1 mm., m.p. 46—48°, reduced (Clemmensen) to the Me_2 *ether*, b.p. 245—248°/0·1 mm., of αβ-*di*-p-*hydroxyphenyloctadecane*, m.p. 86—87° (di-2-naphthoate, m.p. 135—136°). Reduction (Na, EtOH) of (**X**) and subsequent dehydration affords the Me_2 *ether*, b.p. 244—246°/0·1 mm., of 4 : 4′-*dihydroxy*-α-*cetylstilbene*, b.p. 268—275°/0·15 mm. (*di*-2-*naphthoate*, m.p. 95—96°; dibenzoate, m.p. 62—63°). Dehydration of the products from (**X**) and MgRBr gives the Me_2 *ethers*, b.p. 260—264°/0·15 mm. and 238—242°/0·1 mm., of 4 : 4′-*dihydroxy*-α-*ethyl*-, m.p. 90—91°, and -α-n-*amyl*-β-*cetylstilbene*, m.p. 98° (bis-3 : 5-dinitrobenzoate, m.p. 140—141°), respectively. *Benzyldeoxyanisoin*, m.p. 122°, and CH_2Ph·MgCl yield αδ-*diphenyl*-βγ-*dianisylbutan*-β-*ol*, m.p. 113—114°, dehydrated ($KHSO_4$ or Ac_2O–AcCl) and then demethylated to 4 : 4′-*dihydroxy*-αβ-*dibenzylstilbene*, forms, m.p. 181—182° and 160—161°. αα*β-Triphenylbutyl alcohol*, m.p. 93—94° (from CHPhEt·COPh and MgPhBr), is dehydrated ($KHSO_4$) to αα*β-triphenyl*-Δ^α-*butene*, m.p. 80—81°, reduced (Na, EtOH) to αα*β-triphenylbutane*, m.p. 77—78°. αβ-*Diphenyl*-α-*anisylethyl alcohol*, m.p. 112—113° (from *p*-OMe·C_6H_4·CO·CH_2Ph and MgPhBr), gives the *Me ether*, b.p. 175—178°/0·2 mm., of α-p-*hydroxyphenylstilbene*, m.p. 117—118°. Dehydration ($KHSO_4$) of the product from *p*-methoxy-α-ethyldeoxybenzoin and MgPhBr affords α-*anisyl*-β-*methylstilbene*, forms, m.p. 117—118° and 88—89°, both demethylated to α-p-*hydroxyphenyl*-β-*methylstilbene*, m.p. 104—105°. α-*Phenyl*-αβ-*dianisylbutan*-α-*ol*, m.p. 107—108° (prep. by MgPhBr), gives the Me_2 *ether*, m.p. 80—81°, of 4 : 4′-*dihydroxy*-α-*phenyl*-β-*ethylstilbene*, m.p. 177—178°. 2 : 2′-*Dimethoxy*-α-*ethyldeoxybenzoin*, b.p. 167—171°/0·4 mm., m.p. 58° (from the deoxybenzoin and EtI in EtOH–NaOEt), and MgEtBr afford γδ-*di*-o-*anisylhexan*-γ-*ol*, m.p. 103—104°, whence 2 : 2′-*dimethoxy*-, b.p. 140—142°/0·35 mm., m.p. 113—114°, and 2 : 2′-*dihydroxy*-αβ-*diethylstilbene*, m.p. 152—153°. *m*-OH·C_6H_4·COEt is reduced (Al–Hg in moist Et_2O) to 3 : 3′-*dihydroxy*-γδ-*diphenylhexane*-γδ-*diol*, m.p. 145—146° [purified through the *diacetate*, m.p. 158—159° (prep. by boiling Ac_2O–C_5H_5N)], dehydrated (Ac_2O–AcCl) to 3 : 3′-*dihydroxy*-γδ-*diphenyl*-Δ$^{\beta\delta}$-*hexadiene*, m.p. 166—167° (as diacetate, m.p. 85°). 2 : 2′-*Dihydroxy*-γδ-*diphenylhexane*-γδ-*diol*, forms, m.p. 270—271° and 162—163° (obtained similarly from *o*-OH·C_6H_4·COEt), is methylated (Me_2SO_4) to the 2 : 2′-Me_2 ether, forms, m.p. 168—169° and 132—133°, respectively, also obtained by reduction of *o*-OMe·C_6H_4·COEt, and dehydrated to the Me_2 *ether*, m.p. 112—113°, of 2 : 2′-*dihydroxy*-γδ-*diphenyl*-Δ$^{\beta\delta}$-*hexadiene*, m.p. 136—137°. Ethyldeoxyanisoin and PCl_5 at 100° (bath) give α-*chloro*-4 : 4′-*dimethoxy*-β-*ethylstilbene*, b.p. 179—184°/0·1 mm., which could not be demethylated ($AlBr_3$; EtOH–KOH; AcOH–HCl). 4 : 4′-Dibenzoyloxy-α-ethyldeoxybenzoin and PCl_5 afford a *compound*, $C_{30}H_{22}O_4Cl_2$, m.p. 166°, probably OBz·C_6H_3Cl·CEt:CCl·C_6H_4·OBz, converted by hot quinoline into a *substance*, m.p. 182°. Anisoin and PCl_5 lead to anisil; PCl_3 at 100° (bath) gives some α-*chlorodeoxyanisoin*, m.p. 86° (and much P-containing oil) (converted by EtOH into anisoin Et ether, m.p. 105°), whilst PCl_3 followed by PCl_5 at 100° affords αβ-*dichloro*-4 : 4′-*dimethoxystilbene*, m.p. 170°. Benzoin (**XI**), PhCl, and H_2SO_4 at 100°/24 hr. give tetraphenylfuran, m.p. 170°, benzil, and α-p-*chlorophenyldeoxybenzoin*, m.p. 104°; the last with PCl_5 (heat) affords α-*chloro*-β-p-*chlorophenylstilbene*, b.p. 194°/0·1 mm. PhOMe and (**XI**) similarly yield some α-o-, m.p. 91°, and α-p-*anisyldeoxybenzoin*, m.p. 127°, whilst anisoin, PhOMe, and H_2SO_4 at 100° give α-p-*anisyldeoxyanisoin*, b.p. 240°/0·1 mm., converted by *p*-OMe·C_6H_4·MgBr into tetra-anisylethylene, m.p. 188°, which is demethylated to *tetra*-p-*hydroxyphenylethylene*, chars >330°, and a mixture of CO(C_6H_4·OH-*p*)$_2$ and CH_2(C_6H_4·OH-*p*)$_2$. H. B.

Synthesis of œstrogenic indene derivatives. Configuration of stilbœstrol. U. V. Solmssen (*J. Amer. Chem. Soc.*, 1943, **65**, 2370—2375).—The Na salt (prep. by NaOEt–EtOH in Et_2O) of *p*-OMe·C_6H_4·CH_2·CO_2H with *m*-OMe·C_6H_4·CHO in AcOH at 175° (bath) gives m-*methoxy*-α-p-*anisylcinnamic acid* (**I**) (92·2%), m.p. 169°, with some 3 : 4′-*dimethoxystilbene*, m.p. 109—110°, and the *anhydride*, m.p. 120—121° (identified by hydrolysis by hot 5% aq. NaOH), of (**I**). H_2–Pd reduces (**I**) in AcOH to α-p-*anisyl*-β-m-*anisylpropionic acid*, m.p. 106°, which with P_2O_5 in C_6H_6 at room temp. gives 7- (? 5-) (**II**) (34·4%), m.p. 172°, and 5- (? 7-)*methoxy*-2-p-*anisyl*-1-*indanone* (**III**) (34·4%), m.p. 96°. (**II**) does not react with MgEtI (hence suggested orientation), but (**III**) in C_6H_6–Et_2O gives readily a Mg derivative and thence a carbinol, dehydrated by boiling 5% H_2SO_4 to 6-*methoxy*-2-p-*anisyl*-3-*ethylindene* (**IV**) (71·4%), m.p. 87—88° (purified by chromatography). With HBr–AcOH, (**IV**) gives 6-*hydroxy*-2-p-*hydroxyphenyl*-3-*ethylindene* (**V**), unstable in air, m.p. 136° [*diacetate* (**VI**), m.p. 118—120°; *dipropionate* (**VII**), m.p. 88—89°]. H_2–Pd–MeOH and then HBr–AcOH converts (**IV**) into 5-*hydroxy*-2-p-*hydroxyphenyl*-1-*ethylindane* (**VIII**), m.p. 162—163°. Absorption curves (max. at 295 and 297 mμ., respectively) are very similar for (**VI**) and *trans*-stilbene, but those of stilbœstrol (**IX**) and its diacetate are quite different, which renders doubtful the supposed *trans*-configuration of (**IX**). Œstrogenic doses (subcutaneous) relative to (**IX**) are: (**VI**) 11·6, (**VII**) 375, (**V**) 15, (**VIII**) 23·3, œstrone 1·2; oral doses of (**IX**) and (**VI**) are 1 : 60·5. R. S. C.

Aromatic cyclodehydration. XV. 9 : 10-Di-*p*-hydroxyphenylphenanthrene. C. K. Bradsher and L. J. Wissow (*J. Amer. Chem. Soc.*, 1943, **65**, 2304—2305; cf. A., 1944, II, 42).—Benzoin and *o*-C_6H_4Ph·MgI (**I**) (>2 mols.) in C_6H_6 give, after boiling, mixed glycols, cyclised by boiling 48% aq. HBr–AcOH (1 : 1) (2 days) to 9 : 10-diphenylphenanthrene (29%). Anisoin and (**I**) give mixed glycols, converted by hot 48% aq. HBr–AcOH (3 : 2) into (? impure) 9 : 10-di-*p*-hydroxyphenylphenanthrene (**II**) (28%), shrinks at 286—288°, m.p. 296—298° (*diacetate*, m.p. 234°; *dipropionate*, m.p. 185—186°), but with 34% aq. HBr–AcOH gives 9 : 10-*di*-p-*anisylphenanthrene* (**III**) (2%), m.p. 256°. (**III**) (m.p. 256—258°) is obtained by Me_2SO_4–10% NaOH from (**II**) and is reconverted thereinto by HI–AcOH or 42% aq. HBr–AcOH. R. S. C.

Organic derivatives of silicon. LI. Bisdihydroxytetraphenylethane orthosilicate. F. S. Kipping and J. T. Abrams (*J.C.S.*, 1944, 81—84).—$SiCl_4$, Mg, Et_2O, and $COPh_2$ give some *bisdihydroxytetraphenylethane orthosilicate* and mainly (CPh$_2$·O·$SiCl_3$)$_2$, which with H_2O gives variable mixtures of α- and β-benzpinacolins, dihydroxytetraphenylethane, and SiO_2, together in some cases with a little C_2Ph_4. It is inferred that the linkage of Si atoms, under the conditions stated, is brought about by Mg monohalide. F. R. S.

Syntheses in the naphthalene series. I. 1 : 3-Dihydroxynaphthalenes. G. Soliman and R. W. West. (*J.C.S.*, 1944, 53—55).—The Na derivative of CH_2Ph·CO·CH_2·CO_2Et (**I**) and MeI in EtOH afford *Et* γ-*phenyl*-α-*methylacetoacetate*, b.p. 176—178°/18 mm., further methylated to the αα-Me_2 compound, b.p. 180°/22 mm. Similarly prepared are the α-*ethyl*, b.p. 160°/6 mm., -*propyl*, b.p. 164°/6 mm., -iso*propyl*, b.p. 158°/6 mm., -*butyl*, b.p. 172—174°/7 mm., -iso*butyl*, b.p. 172—174°/7 mm., and -iso*amyl* analogue, b.p. 152°/2 mm. Conc. H_2SO_4 first at 0° and then at room temp. converts (**I**) into 1 : 3-$C_{10}H_6$(OH)$_2$, m.p. 118—120°, and traces of CH_2Ph·COMe and CH_2Ph·CO_2H. Similarly prepared are 1 : 3-*dihydroxy*-2-*methyl*-, m.p. 139—140° (*diacetate*, m.p. 118°), -2-*ethyl*-, m.p. 126—128° (*diacetate*, m.p. 82°), -2-*propyl*-, m.p. 103° (*diacetate*, m.p. 75°), -2-*iso*propyl- (impure) (*diacetate*, m.p. 75°), -2-*butyl*-, m.p. 108—110° (*diacetate*, m.p. 65°), -2-*iso*butyl- (impure) (*diacetate*, m.p. 135°), and -2-iso*amyl*-*naphthalene*, m.p. 92—93° (*diacetate*, m.p. 79—80°; *dibenzoate*, m.p. 108—109°). 2 : 1 : 3-$C_{10}H_5$Ph(OH)$_2$ or 1 : 3 : 2-(OH)$_2$$C_{10}H_5$·$CO_2$Et is obtained from cold H_2SO_4 and CH_2Ph·CO·CHPh·CO_2Et or CH_2Ph·CO·CH(CO_2Et)$_2$, respectively. *p*-NO_2·C_6H_4·CH_2·COCl and CHAcNa·CO_2Et in boiling C_6H_6 give after hydrolysis with aq. NH_3 *Et* γ-p-*nitrophenylacetoacetate*, m.p. 82° [dil. H_2SO_4 yields *p*-NO_2·C_6H_4·CH_2·COMe (**II**)], converted by cold H_2SO_4 (3 days) into γ-4-*nitrophenylacetoacetic acid*, m.p. 116° (decomp.) [hot H_2O gives (**II**)]. A. T. P.

Labile union of oxygen with carbon. Relations between resonance in the anthracene system and the labile state of oxygen in photo-oxides. C. Dufraisse, R. Demuynck, and A. Allais (*Compt. rend.*, 1942, **215**, 487—489).—Consideration of resonance in the anthracene system indicates that the photo-oxide (**I**) of 2 : 3-dimethoxy-5 : 10-diphenylanthracene should dissociate only slightly less readily than that (**II**) of the corresponding 1 : 4-compound; this is verified experimentally, (**I**) dissociating at a slightly higher temp. (120°) than (**II**). The photo-oxide of 5 : 10-diphenylanthracene dissociates at 180°; those of the 1- and 2-OMe-derivatives dissociate at 150° and 160°, respectively, and the photo-oxide of the 1 : 8-(OMe)$_2$-compound dissociates at 215°. These facts support the authors' views on the participation in the resonance effects of electrons from OMe groups. A. J. E. W.

Keten acetals. XIII. Cyclic trimerisation of keten diethyl acetal by hydrogen fluoride: 1 : 1 : 3 : 3 : 5 : 5-hexaethoxy*cyclo*hexane. S. M. McElvain and J. W. Langston (*J. Amer. Chem. Soc.*, 1943, **65**, 2239—2241; cf. A., 1944, II, 144).—Adding HF (0·25 g.) in Et_2O

(25 ml.) to $CH_2{:}C(OEt)_2$ (I) (25 g.) in Et_2O (2·5 l.) and keeping for 7—14 days gives 1 : 1 : 3 : 3 : 5 : 5-*hexaethoxycyclohexane* (II), m.p. 72—74°, and the dimeride (A., 1940, II, 202) of (I) (cf. A., 1942, II, 216). (II) gradually loses EtOH when kept; the change is very greatly accelerated by acid and, in order to obtain (II), all glassware must be washed with NaOH. Distilling (II) with a trace of conc. H_2SO_4 gives EtOH (100% of 3 mols.) and *s*-$C_6H_3(OEt)_3$ (83%). Adding solid CO_2 to (II) in aq. EtOH gives 83% of *s*-$C_6H_3(OEt)_3$. $CHMe{:}C(OEt)_2$ and HF give $EtCO_2Et$ and EtF. R. S. C.

Rearrangement of 2-allyloxychrysene. C. K. Bradsher and S. T. Amore (*J. Amer. Chem. Soc.*, 1943, **65**, 2466).—2-Chrysenol (prep. improved to give a 86% yield; cf. Newman *et al.*, A., 1941, II, 38), $CH_2{:}CH{\cdot}CH_2Br$, and K_2CO_3 in $COMe_2$ give *2-allyloxychrysene* (63%), m.p. 110—111°, which with Ac_2O–$NPhMe_2$ at 160—180° gives *2-acetoxy-1-allylchrysene* (87%), m.p. 103°. R. S. C.

Unexpected rearrangement in the application of the Skraup reaction to 3-nitro-4-aminoveratrole. K. C. Frisch, M. Silverman, and M. T. Bogert (*J. Amer. Chem. Soc.*, 1943, **65**, 2432—2434).—3 : 1 : 2 : 4-$NO_2{\cdot}C_6H_2(OMe)_2{\cdot}NH_2$ (I) (prep. modified; cf. Pisovschi, A., 1910, i, 643; *Ac* derivative, m.p. 150·5°) gives no quinoline by the Skraup reaction using As_2O_5 or $PhNO_2$ and dil. or conc. H_2SO_4; use of glycerol–As_2O_5 in 85% H_3PO_4 gives 30% of 5 : 1 : 2 : 4-$NO_2{\cdot}C_6H_2(OMe)_2{\cdot}NH_2$ (II). The As_2O_5 and glycerol may be omitted, as (I) in hot 85% H_3PO_4 + AcOH at 140—160° (not in boiling tetrahydronaphthalene) gives up to 30% of (II). Prep. of (II) from 1 : 2 : 4-$(OMe)_2C_6H_3{\cdot}NHAc$, of 1 : 2 : 4 : 5-$(OMe)_2C_6H_2(NH_2)_2$, m.p. 131° (*picrate*, m.p. 192°; Ac_2 derivative, m.p. 204—205°), 2 : 3-*diphenyl*-5 : 6-, m.p. 139—140°, and -6 : 7-*dimethoxyquinoxaline*, m.p. 251—252°, is described. Temp. are corr. R. S. C.

Unsymmetrical diacyl derivatives of 4 : 4′-diaminodiphenyl sulphone. H. A. Shonle and A. M. Van Arendonk (*J. Amer. Chem. Soc.*, 1943, **65**, 2375—2377).—In parentheses below, activities against *Streptococcus* > that of sulphanilamide and against *Pneumococcus* type I > that of sulphapyridine are indicated * and †, respectively. $(RCO)_2O$ (I) and $SO_2(C_6H_4{\cdot}NH_2\text{-}p)_2$ (*†) (1 mol.) in boiling dioxan give *p*-$NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}C_6H_4{\cdot}NH{\cdot}COR\text{-}p$ (R = Me, m.p. 232—233°, Et, m.p. 201—202°, and Pr^a, m.p. 192—193°) [and some $SO_2(C_6H_4{\cdot}NH{\cdot}COR\text{-}p)_2$], converted by R′COCl in C_5H_5N at 80° into *p*-$COR{\cdot}NH{\cdot}C_6H_4{\cdot}SO_2{\cdot}C_6H_4{\cdot}NH{\cdot}COR'\text{-}p$, the following being thus prepared: 4-acetamido-4′-propion-, m.p. 227—228° (*), -*n*-butyr-, m.p. 223·4° (*), -n-*hexo*-, m.p. 197—198°, -n-*deco*-, m.p. 176—178°, -n-*dodeco*-, m.p. 168—170°, -n-*tetradeco*-, m.p. 164—165°, -n-*hexadeco*-, m.p. 158—160°, -n-*octadeco*-, m.p. 157—162°, -*croton*-, m.p. 231—232° (*), -*H malein*- (? *fumar*-), m.p. 230—231°, -*cinnam*-, m.p. 180—181°, -*chloroacet*-, m.p. 214—215° (*), -*trichloroacet*-, m.p. 268—270° (*), -*pyridine*-2-*carboxyl*-, m.p. 282—283°, -benz-, m.p. 212—213°, -p-*nitrobenz*-, m.p. 239—240°, and -2-*furo*-, m.p. 240—241°, -*amidodiphenyl sulphone*; 4-propionamido-4′-butyr-, m.p. 201—202° (*†), -*H malein*- (? *fumar*-), m.p. 223—224° (*), and -*chloroacet*-, m.p. 201—202° (*), -*amidodiphenyl sulphone*; 4-n-*butyramido*-4′-*chloroacetamidodiphenyl sulphone*, m.p. 178—179° (*). R. S. C.

2 : 5-Dihydroxybenzyl [gentisyl] alcohol, m.p. 100° (dimethyl ether, b.p. 140°/3·3 mm.).—See A., 1944, III, 290.

Amino-alcohols. XII. Optical isomerides in the ephedrine series of compounds. C. Jarowski and W. H. Hartung (*J. Org. Chem.*, 1943, **8**, 564—571).—The mixture of bases obtained by reduction of $OH{\cdot}CHPh{\cdot}CHMe{\cdot}NO_2$ is separated into *dl*- and *dl*-*ψ*-propadrine by crystallisation of the hydrochlorides from abs. EtOH. The bases are separated into their optical isomerides by use of the optically active mandelic acids in EtOH or, sometimes, *sec.*-BuOH. Thus are obtained: (−)-ephedrine (−)-mandelate, m.p. 170°, $[\alpha]_D^{5\cdot5}$ −70·6° ([α] of all salts are in H_2O), and (+)-mandelate, m.p. 78—91°, $[\alpha]_D^{25\cdot5}$ +21·3°; (−)-propadrine, m.p. 171·5—172°, $[\alpha]_D^{29}$ −70·6°, and (+)-propadrine, m.p. 164·5—165°, $[\alpha]_D^{29}$ −42·8°, (−)-mandelate; (+)-propadrine (+)-mandelate, m.p. 171·5—172°, $[\alpha]_D$ +70·7°; *dl*-propadrine *dl*-mandelate, m.p. 161—162°; (+)-*ψ*-propadrine, m.p. 170°, $[\alpha]_D^{32\cdot4}$ −45·3°, and (−)-*ψ*-propadrine, m.p. 163·5°, $[\alpha]_D^{3\cdot4}$ −41·3, (−)-mandelate; *dl*-*ψ*-propadrine *dl*-mandelate, m.p. 162·5—163°; (+)-benzedrine, m.p. 162—163°, $[\alpha]^{25}$ −50·0°, and (−)-benzedrine, m.p. 166°, $[\alpha]_D^{26}$ −68·6°, (−)-mandelate; (−)-benzedrine (+)-mandelate, m.p. 163°, $[\alpha]_D^{28}$ +49·8°; *dl*-benzedrine *dl*-mandelate, m.p. 156·5°; (−)-*β*-phenylpropylamine (−)-mandelate, m.p. 127—127·5°, $[\alpha]_D^{\cdot6}$ −57·8°; (+)-*β*-phenylpropylamine (+)-mandelate, m.p. 127—127·5°, $[\alpha]_D^{29\cdot8}$ +58·7°, and (−)-mandelate, m.p. 118·5—119°, $[\alpha]_D^{29\cdot8}$ −47·5°; *dl*-*β*-phenylpropylamine *dl*-mandelate, m.p. 119·5—120·5°; *dl*-phenylethanolamine *dl*-mandelate, m.p. 129·5—130°; (−)-phenylethanolamine (−)-mandelate, m.p. 144—145°, $[\alpha]_D^{31}$ −58·3°. The following consts. are recorded: (−)-ephedrine, m.p. 34—40°, $[\alpha]_D^{27}$ −3·47° in abs. EtOH (the same solvent for all this series); (−)-, m.p. 102°, $[\alpha]^{30}$ −19·90°, and (+)-propadrine, m.p. 102°, $[\alpha]_D^{32}$ +20·80°; (+)-, m.p. 179°, $[\alpha]_D^{29}$ +41°, and (−)-*ψ*-propadrine hydrochloride, m.p. 178°, $[\alpha]_D^{32}$ −38·7°; (+)-, $[\alpha]_D^{25}$ +3·8°, and (−)-benzedrine, $[\alpha]^{28}$ −3·8°; (−)-, $[\alpha]_D$ −18·82°, and (+)-, $[\alpha]$ +18·8°, -*β*-phenylpropylamine; (−)-phenylethanolamine, $[\alpha]^{30}$ −20·90°. Solubilities of the diastereoisomeric mandelates in H_2O and normal saline at 37° and 25° are recorded. Pharmacological data for many mandelates are recorded. From the data it appears that the optimum configuration for activity is found in those isomerides in which C attached to Ph, if asymmetric, is lævorotatory and in which the carbamine-C, if asymmetric, is dextrorotatory. In all cases except that of the *ψ*-propadrines the isomeride forming the less sol. mandelate is the more active physiologically. An isosteric analogy between $CHPhMe{\cdot}CH_2{\cdot}NH_2$ and $OH{\cdot}CHPh{\cdot}CH_2{\cdot}NH_2$ is indicated. H. W.

Inhibition of oxidation of adrenaline by malonic acid.—See A., 1944, III, 250.

Tautomerism of indene. C. F. Koelsch and R. A. Scheiderbauer (*J. Amer. Chem. Soc.*, 1943, **65**, 2311—2314).—A fixed position for the Δ^2-ethylenic linking of indene derivatives is indicated by the prep. of isomeric 5- and 6-substituted derivatives. H_2–PtO_2 in EtOH reduces crude 6-nitro- to 6-amino-1-indanone (47—54%), m.p. 168—171°, which, when diazotised as sulphate and then added to hot 30% H_2SO_4, gives 6-hydroxy-1-indanone (50—70%), m.p. 151—153°. Adding this and then $CH_2Br{\cdot}CO_2Et$ to NaOEt–EtOH and warming gives *Et* 1-*keto*-6-*indanyloxyacetate* (I) (76%), m.p. 111—112°. With warm 10% KOH, (I) gives a (?) polymeric *acid*, m.p. 227—229°, but with 15% H_2SO_4 gives 1-*keto*-6-*indanyloxyacetic acid* (80%), m.p. 161·5—162·5°. (I) gives an unstable phenylhydrazone, m.p. 113—115°, reduced by H_2–Raney Ni in EtOH at 140° to NH_2Ph (44%) and 1-*amino*-6-*indanyloxyacetic acid* (39—40%), sinters ~225°, decomp. 269° [*Et* ester *hydrochloride* (+EtOH) (II), m.p. 171—172°]. Hydrogenation (Pd-black) of the *oxime*, m.p. 130·5—132°, of (I) in EtOH or HCl–EtOH gives impure products, but in Ac_2O yields *Et* 1-*acetamido*-6-*indanyloxyacetate*, m.p. 116—117°, also obtained from (II) by Ac_2O–NaOAc. Hydrogenation (Raney Ni) of (I) in EtOH, at 105°/1175 lb. gives an oil, which with 10% KOH yields 1-*hydroxy*-6-*indanyloxyacetic acid*, $+H_2O$ (67%), m.p. 82—84°, effervesces and resolidifies at 105°, remelts 147—150°, but, when distilled over a little $KHSO_4$, is dehydrated to *Et* 5-*indenyloxyacetate* (III) (63—78%), m.p. 48—48·5°, b.p. 200—205°/30 mm. With dil. KOH, (III) gives a mixture and with 10% H_2SO_4 a resin, but with boiling 2% Na_2CO_3 it gives 5-*indenyloxyacetic acid* (IV) (85—89%), m.p. 118—119°, hydrogenated (Pt-black) in EtOH to 5-*indanyloxyacetic acid*, m.p. 154—155°. Boiling 5% KOH isomerises (IV) to 6-*indenyloxyacetic acid* (11%), m.p. 140·5—143°, and polymers. *p*-$OMe{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CO_2Et$ (prep. from *p*-$OMe{\cdot}C_6H_4{\cdot}CHO$, EtOAc, NaOEt, and a little EtOH in 58—61% yield) resists H_2–Cu chromite; the derived acid is reduced electrolytically to *p*-$OMe{\cdot}C_6H_4{\cdot}[CH_2]_2{\cdot}CO_2H$, the Et ester, b.p. 158—162°/22 mm., of which gives only resins with $Et_2C_2O_4$.

p-$OMe{\cdot}C_6H_4{\cdot}[CH_2]_2{\cdot}COCl$ and $AlCl_3$ in $PhNO_2$ give 3—17% (lit. 20%) of 6-methoxy-1-indanone and in C_6H_6 gives *p*-$OMe{\cdot}C_6H_4{\cdot}[CH_2]_2{\cdot}COPh$ (44—59%). 2-$C_{10}H_7{\cdot}[CH_2]_2{\cdot}CO_2Et$ gives a $CO{\cdot}CO_2Et$ derivative (44—63%), which in 80% H_2SO_4 at 85° and then boiling 10% NaOH gives 4 : 5-*benzindene*-2-*carboxylic acid* (31—40%), m.p. 263—265° (decomp.), decarboxylated by $Cu(OAc)_2$ in quinoline at 220—240° to 4 : 5-*benzindene* (45—85%), m.p. 48·5—50°, b.p. 173°/33 mm. (*picrate*, m.p. 125—127°). 7-Hydroxy-4-methyl-1-indanone (V) resists Na–EtOH or $-C_5H_{11}{\cdot}OH$ and H_2–Cu chromite, and its benzoate resists H_2–catalyst. With $CH_2Br{\cdot}CO_2Et$ and NaOEt in EtOH, (V) gives *Et* 1-*keto*-4-*methyl*-7-*indanyloxyacetate* (VI) (70—85%), m.p. 124·5—125·5°, hydrolysed by aq. KOH to the corresponding *acid*, m.p. 200—203°. H_2–Raney Ni at 140—175°/100 atm. reduces (VI) to an oil, which in 10% KOH gives 4-*methyl*-7-*indanyloxyacetic acid* (36—41%), m.p. 191—192°, but at 100° gives a mixture, whence hydrolysis yields 1-*hydroxy*-4-*methyl*-7-*indanyloxyacetic acid* (46—56%), m.p. 122—123° (decomp.). The *oxime*, m.p. 186—187° (gas), of (VI) resists H_2–Pt-black in dioxan; the *phenylhydrazone*, m.p. 163—166°, with H_2–Raney Ni in EtOH at 100°/100 atm. gives the *lactam* (36%), m.p. 241—241·5°, of 1-amino-4-methyl-7-indanyloxyacetic acid. R. S. C.

Restricted rotation in arylolefines. VIII. Synthesis and resolution of *β*-substituted *β*-arylacrylic acids. R. Adams and C. W. Theobald (*J. Amer. Chem. Soc.*, 1943, **65**, 2383—2387; cf. A., 1944, II, 98).—2 : 4 : 6 : 3 : 1-$C_6HMe_3Br{\cdot}COMe$ (I) (prep. improved to give a 74% yield) with HNO_3 (*d* 1·5) at 0° gives the 5-NO_2-derivative, m.p. 119—120°, and with PCl_5–$POCl_3$–PCl_3 at 65° (17 hr.) and then 90° (1 hr.) gives *α-chloro-α-bromomesitylethylene* (II) (63%; not obtainable pure under other conditions of prep.), b.p. 109—110°/0·3 mm., *ω-chloroacetobromomesitylene* (11·5%), m.p. 64—65°, and an impure phosphate (8·5%), m.p. 209—212°, of the enolic form of (I). With boiling NaOEt–EtOH (not $NaNH_2$ in xylene or alkali in aq. EtOH), (II) gives *bromomesitylacetylene* (III) (57%), b.p. 84°/0·2 mm. (Hg salt, m.p. 255°). *Bromomesitylpropiolic acid* (IV) (63%) (prep.; *loc. cit.*), m.p. 168—169°, also obtained, less well, from 2 : 4 : 6 : 3 : 1-$C_6HMe_3Br{\cdot}CCl{:}CH{\cdot}CO_2H$ (V) by hot 10% aq. NaOH, with AcOH–HCl gives 86% of (V) (cf. A., 1942, II, 93), the active form of which has a half-life period = 200 min. in boiling $Bu^{\alpha}OH$. HBr adds to (IV) in AcOH at 65—70°, giving *β-bromo-β-bromomesitylacrylic acid* (VI) (83%), m.p. 158·5—159·5°, which with quinine in EtOH yields the l-, m.p. 155—155·5°, $[\alpha]_D^{25}$ −37·2° in EtOH [*quinine* salt, m.p.

175° (decomp.), $[\alpha]_D^{26}$ −83·2° in EtOH; half-life period = 64 hr.], and d-*acid*, m.p. 155—156°, $[\alpha]_D^{28}$ +33·6° in EtOH [*quinine* salt, m.p. 164—164·5° (decomp.), $[\alpha]_D^{28}$ −48·1° in EtOH]. With MgEtBr and then $ClCO_2Me$ in boiling Et_2O, (**III**) gives *Me bromomesitylpropiolate* (52%), m.p. 83·5—85° (and a *substance*, $C_{13}H_{13}Br$, m.p. 160—161°), which with NaOMe in boiling MeOH affords *Me β-methoxy-β-bromomesitylacrylate* (**VII**) (60%), m.p. 78—79·5°, also obtained by CH_2N_2 from 2 : 4 : 6 : 3 : 1-$C_6HMe_3Br{\cdot}CO{\cdot}CH_2{\cdot}CO_2H$, m.p. 114—115° (decomp.) (lit., 98—99°). Boiling KOH–EtOH–H_2O hydrolyses (**VII**) to *β-methoxy-β-bromomesitylacrylic acid* (**VIII**), m.p. 156—157° (decomp.), which could not be resolved and yields non-mutarotating *quinine*, $[\alpha]_D^{27}$ −87·3° in EtOH, and l-*brucine* salts, $[\alpha]_D^{30}$ −37·5° in EtOH. The Cl and CO_2H of (**V**) and (**VI**) are *trans*, but the OMe and CO_2H of (**VIII**) are probably *cis*. 2 : 3 : 4 : 6 : 1-$C_6HMe_4{\cdot}CCl{:}CH{\cdot}CO_2H$ is resolved by quinine in EtOAc to the d-, m.p. 184—185°, $[\alpha]_D^{26}$ +35·7° in EtOH [*quinine* salt, m.p. 163—165° (decomp.), $[\alpha]_D^{28}$ −59·6° in EtOH], and l-acid, m.p. 184—185°, $[\alpha]_D^{25}$ −35·7° in EtOH [*quinine* salt, m.p. 193—194° (decomp.), $[\alpha]_D^{28}$ −84·0° in EtOH; half-life period = 174 min.]. M.p. are corr. R. S. C.

Interaction of sodium triphenylmethyl with esters of acetylenic acids. E. G. Lindstrom and W. D. McPhee (*J. Amer. Chem. Soc.*, 1943, **65**, 2387—2389).—Adding $CMe{:}C{\cdot}CO_2Et$, b.p. 162—164°, to $NaCPh_3$ (>1 mol. consumed) gives *aaaεεε-hexaphenyl-δ-methyl-Δ^γ-n-penten-β-one* (**I**) (53%), m.p. (from C_6H_6–light petroleum) 226—227° or (from AcOH) 226—230·5°, and the Et ester of *β-triphenylmethylcrotonic acid* (**II**) (24%), sinters 245°, m.p. 256—257° (decomp.). The reverse addition gives 23% of crude (**I**), 28% of (**II**), and 45% of $CHPh_3$. The structure of (**II**) is proved by oxidation ($KMnO_4$–KOH–H_2O; 100°) to $CPh_3{\cdot}COMe$ (or, in one experiment, $CPh_3{\cdot}OH$). (**II**) resists H_2–Raney Ni or H_2–PtO_2 at 75°/60 lb. and is not obtained from $CPh_3{\cdot}COMe$ by $CH_2Br{\cdot}CO_2Et$ and Zn. Conc. HCl–MeOH converts (**II**) into its *Me* ester, m.p. 162·5—163·5°, which with $NaCPh_3$ (excess) in Et_2O gives (**I**) (proof of structure). $CEt{:}C{\cdot}CO_2Et$, b.p. 78—80°/16—18 mm., and $NaCPh_3$ give similarly *aaa-triphenyl-δ-triphenylmethyl-Δ^γ-n-hexen-β-one* (**III**) (70%), m.p. 201—202°, and, after hydrolysis, *γ-triphenylmethyl-Δ^α-n-pentenoic acid* (16%), sinters 208°, m.p. 215—217° [*Me* ester, m.p. 170—171°, with $NaCPh_3$ gives (**III**)]. R. S. C.

Chloromethylation of tetrahydronaphthalene. Synthesis of β-5-tetrahydronaphthylpropionic acid. R. T. Arnold and R. Barnes (*J. Amer. Chem. Soc.*, 1943, **65**, 2393—2395).—Adding conc. H_2SO_4 to tetrahydronaphthalene, 40% CH_2O, and conc. HCl at 60—65° during 5—6 hr. gives a mixture (**I**), b.p. 110—114°/3 mm., of 5- and 6-CH_2Cl derivatives, which when freshly prepared is reduced by H_2–Pd–$BaSO_4$ in EtOH at 45 lb. to 5- + 6-methyl-1 : 2 : 3 : 4-tetrahydronaphthalenes (*A*), but, after being kept for several days, polymerides which have formed poison the catalyst. (*A*) with S at the b.p. give 1- + 2-$C_{10}H_7Me$, whence CrO_3 yields 1 : 2 : 4-$O{:}C_{10}H_5Me{:}O$. With $CHNa(CO_2Et)_2$–EtOH, (**I**) gives esters, b.p. 150—155°/2 mm., which by hydrolysis (KOH–MeOH–H_2O) and decarboxylation (180°) give acids, whence light petroleum–C_6H_6 yields *β*-1 : 2 : 3 : 4-tetrahydro-5-naphthylpropionic acid (**II**), m.p. 136—137°, and a eutectic mixture, m.p. 72°, thereof with its 6-isomeride (**III**). $SOCl_2$–C_6H_6–C_5H_5N at room temp. and then $SnCl_4$–$PhNO_2$ at 0° and later 30—35° converts (**II**) into 4 : 5-*tetramethylene-1-indanone* (81%), m.p. 63—64·5°, reduced by Zn–Hg–HCl–H_2O–AcOH–PhMe to 4 : 5-tetramethyleneindane, m.p. 107·5—108·5° (lit., 109—110°). S at 225—250° dehydrogenates (**II**) to 1-$C_{10}H_7{\cdot}[CH_2]_2{\cdot}CO_2H$, m.p. 151—152°. 6-Propionyl-1 : 2 : 3 : 4-tetrahydronaphthalene with S and H_2S in aq. NH_3–dioxan at 165° and then hot aq. KOH gives (**III**), m.p. 81·5—82·5° (cf. Newman *et al.*, A., 1943, II, 300), the Me ester, b.p. 165—168°/12 mm., of which with S at 235—250° and then KOH–MeOH–H_2O gives 2-$C_{10}H_7{\cdot}[CH_2]_2{\cdot}CO_2H$, m.p. 134—135°. R. S. C.

Preparation of benz-*p*-aminoanilide. C. E. Spencer (*J. Amer. Chem. Soc.*, 1943, **65**, 2470—2471).—*p*-$NO_2{\cdot}C_6H_4{\cdot}NHBz$ with H_2–Pt-black (from PtO_2) and a little $FeSO_4$ in EtOH at 56°/50 lb. gives 90% of *p*-$NH_2{\cdot}C_6H_4{\cdot}NHBz$, m.p. 129° (corr.). R. S. C.

Poly*iso*propylbenzenes. IV. Bromo-derivatives, nitriles, amides, and carboxylic acids. A. Newton (*J. Amer. Chem. Soc.*, 1943, **65**, 2441—2443).—By the method of Fuson *et al.* (A., 1941, II, 223) (no replacement occurs), *m*-$C_6H_4Pr^{\beta}_2$ gives the 4- (**I**) (77%) and 2-*Br*-, *p*-$C_6H_4Pr^{\beta}_2$ gives the 2-*Br*-, 1 : 2 : 4-$C_6H_3Pr^{\beta}_3$ gives the 5-*Br*- (also obtained from 1 : 2 : 4 : 5-$C_6H_2Pr^{\beta}_3{\cdot}SO_3H$), and *s*-$C_6H_3Pr^{\beta}_3$ gives the 2-Br-derivative. With CuCN (1·1 mols.) in C_5H_5N at 220°, these Br-compounds give 2 : 4-*di*- [81·9%; also obtained in 36·5% yield from the amine, thus proving the structure of (**I**)], 2 : 5-*di*- (**II**) (75·9%), 2 : 4 : 5-*tri*- (**III**) (requires 2·1 mols. of CuCN and 245° for its prep.; 84·9%), m.p. 43·5—44·5°, and 2 : 4 : 6-*tri*-iso*propylbenzonitrile* (82%). KOH–BuOH–H_2O (a little) at the b.p. then yields 2 : 4-*di*-, m.p. 157·9—158·3°, 2 : 5-*di*-, m.p. 143·7—144·4°, 2 : 4 : 5-*tri*-, m.p. 189—189·6°, and 2 : 4 : 6-*tri*-iso*propylbenzamide* (**IV**), m.p. 218·7—219·3°, and thence (10% NaOH; 200°) the corresponding *acids*, m.p. 107·8—108·2°, 70·5—71·2°, 162·2—163·2°, —, respectively. (**IV**) resists hydrolysis. (**II**) is not hydrolysed by H_2SO_4 at 100° or H_3PO_4 at 160° and only very slowly by boiling EtOH–KOH. 70% HNO_3 (1·44 mols.) in H_2SO_4 at 5—10° converts (**II**) or (**III**) into 5-*nitro*-2 : 4-*diiso*propylbenzonitrile, m.p. 107·3—108°. Physical data are given for the oily products. R. S. C.

Basic-alkyl esters of *p*-aminoalkylbenzoic acids. I, II. F. F. Blicke and W. M. Lilienfeld (*J. Amer. Chem. Soc.*, 1943, **65**, 2281—2284, 2377—2378).—I. Esters, *p*-$NH_2{\cdot}[CH_2]_x{\cdot}C_6H_4{\cdot}CO_2{\cdot}[CH_2]_y{\cdot}NRR'$ (x = 1—3; y = 2—4), are prepared but, with one exception, are pharmacologically of no val. *p*-$C_6H_4Me{\cdot}CO_2H$ [prep. from *p*-$C_6H_4Me{\cdot}CN$ (**I**) by NaOH–H_2O–EtOH; 96% yield] gives ($SOCl_2$) *p*-$C_6H_4Me{\cdot}COCl$ (92%), b.p. 117—120°/24 mm., which with Cl_2 at 120—130° in light gives *p*-$CH_2Cl{\cdot}C_6H_4{\cdot}COCl$ (89%), b.p. 155—160°/35 mm., converted by boiling EtOH containing a few drops of C_5H_5N into *p*-$CH_2Cl{\cdot}C_6H_4{\cdot}CO_2Et$ (90%), b.p. 140—150°/15 mm. With NaI in boiling $COMe_2$ this gives *p*-$CH_2I{\cdot}C_6H_4{\cdot}CO_2Et$, which with $(CH_2)_6N_4$ in boiling $CHCl_3$ yields a cryst. complex (**II**), converted by boiling conc. HCl–EtOH into *p*-$NH_2{\cdot}CH_2{\cdot}C_6H_4{\cdot}CO_2H$ (**III**) (64%), darkens >270°, m.p. >360°, which is also obtained (50%) from (**I**) by, successively, Cl_2, $(CH_2)_6N_4$, and HCl–EtOH. *p*-$Br{\cdot}[CH_2]_2{\cdot}C_6H_4{\cdot}COMe$ and NaOBr give *p*-$Br{\cdot}[CH_2]_2{\cdot}C_6H_4{\cdot}CO_2H$ (80·5%) and thence the acid chloride, amide (97%), and (by $SOCl_2$) nitrile (68%), m.p. 49—50°, b.p. 148—151°/5 mm.; further treatment as above then yields p-*β-aminoethylbenzoic acid* (**IV**) (52%). $Ph{\cdot}[CH_2]_3{\cdot}Br$, AcCl, and $AlCl_3$ in CS_2 at 0° give p-*γ-bromopropylacetophenone* (85·5%), b.p. 160—164°/7 mm., and thence, as above, p-*γ-bromo-* (78%), m.p. 118—120° (*nitrile*, b.p. 153—157°/4 mm.), and p-*γ-amino*-n-*propylbenzoic acid* (**V**), decomp. >290°. Structures of (**IV**) and (**V**) are proved by oxidation to *p*-$C_6H_4(CO_2H)_2$. With boiling $SOCl_2$ and HCl–Et_2O, (**III**)—(**V**) give p-*aminomethyl-*, p-*β-aminoethyl-*, and p-*γ-aminopropyl-benzoyl chloride hydrochloride*, which with $OH{\cdot}[CH_n]_2{\cdot}NRR'$,HCl in boiling $PhMe–(CH_2Cl)_2$ give (*a*) *β-diethylamino-*, m.p. 187—189°, and *β-piperidino-ethyl*, m.p. 233—235°, *γ-piperidino-*, m.p. 228—230°, and *γ-morpholino-n-propyl*, m.p. 218—220° (decomp.), p-*aminomethylbenzoate dihydrochloride*, (*b*) *β-piperidinoethyl*, m.p. 222—225°, *γ-piperidino-*, m.p. 188—190°, and *γ-morpholino*-n-*propyl*, m.p. 190—192°, and *γ-piperidino-ββ-dimethyl*-n-*propyl*, m.p. 248—250° (decomp.), p-*β-aminoethylbenzoate dihydrochloride*, and (*c*) *γ-dibutylamino-*, m.p. 200—202°, *γ-piperidino-*, m.p. 168—170°, and *γ-morpholino*-n-*propyl*, m.p. 193—195°, and *γ-piperidino-ββ-dimethyl*-n-*propyl*, m.p. 196—199°, p-*γ-amino*-n-*propylbenzoate dihydrochloride*. In boiling anhyd. HCl–EtOH, (**II**) gives *p*-$NH_2{\cdot}CH_2{\cdot}C_6H_4{\cdot}CO_2Et$, b.p. 145—148°/8 mm. In boiling EtOH–C_6H_6, the above acid chlorides give *Et* p-*aminomethyl-*, m.p. 235—237°, *p-β*-aminoethyl- (**VI**), m.p. 178—180°, and p-*γ-amino*-n-*propyl-benzoate hydrochloride*, m.p. 174—176°. None of the esters has anæsthetic action and only (**VI**) has definite (weak) pressor action.

II. Adding $AlCl_3$ to *p*-$NHAc{\cdot}[CH_n]_2{\cdot}Ph$ and AcBr in $(CHCl_2)_2$ at 0° and then boiling gives p-*β-acetamidoethylacetophenone* (74%), m.p. 99—101°, b.p. 214—216°/3 mm., converted by NaOBr in aq. dioxan at 0° into *β*-p-*acetamido-* (78%), m.p. 173—175°, and thence by conc. HCl into *p-β*-amino-ethylbenzoic acid (62%).
$NHAc{\cdot}CHMe{\cdot}CH_2Ph$, m.p. 88—91° (lit., 93°), b.p. 144—145°/2 mm., gives similarly p-*β-acetamido*-n-*propylacetophenone* (77%), m.p. 97—99°, b.p. 206—208°/3 mm., p-*β-acetamido-* (84·5%), m.p. 208—210°, and p-*β-amino*-n-*propylbenzoic acid* (59%), decomp. from ~290° (*chloride hydrochloride*; *Et* ester *hydrochloride*, m.p. 140—142°; *β-piperidinoethyl*, m.p. 218—220°, *γ-piperidino-*, m.p. 255—257°, and *γ-morpholino*-n-*propyl*, m.p. 251—253°, and *γ-piperidino-ββ-dimethyl*-n-*propyl*, m.p. 223—226°, ester *dihydrochloride*). The esters have little or no anæsthetic or pressor action. R. S. C.

Synthesis of alkyl and dialkylaminoalkyl esters of 4-fluoro-3-aminobenzoic acid. L. S. Fosdick and A. F. Dodds (*J. Amer. Chem. Soc.*, 1943, **65**, 2305—2306).—M.p. in parentheses below are those of the *hydrochlorides*. 3 : 4 : 1-$NO_2{\cdot}C_6H_3F{\cdot}COCl$ (prep. from the acid by $SOCl_2$), m.p. 23·5—25°, and ROH give *Me*, m.p. 60—61°, Et, m.p. 47—48° (lit., 45·3°), *Pr*^{α}, b.p. 147—157°/4 mm., *Bu*^{α}, b.p. 190—200°/35 mm., dimethyl- (m.p. 168—169°), diethyl- (m.p. 142—143°), dipropyl- (m.p. 123—124°), and dibutyl-aminoethyl (m.p. 80—82°), diethyl- (m.p. 145—147°), dipropyl- (m.p. 140—141°), and dibutyl-aminopropyl (m.p. 83—84°) 4-fluoro-3-nitrobenzoate, reduced by H_2–PtO_2 to *Me*, m.p. 123—126°, *Et*, b.p. 140—145°/5 mm., *Pr*^{α}, m.p. 24—26°, *Bu*^{α}, m.p. 155—160° (decomp.), dimethyl- (**I**) (m.p. 170—172°), diethyl- (m.p. 138—140°), dipropyl- (m.p. 119—120°), and dibutyl-aminoethyl, diethyl- (m.p. 138—142°), dipropyl- (m.p. 145—148°), and dibutyl-aminopropyl (m.p. 136—138°) 4-fluoro-3-aminobenzoate, respectively. The NH_2-esters, except (**I**), are potent anæsthetics, are generally one third to one half as toxic as procaine, but are unstable. R. S. C.

Vicinal substituted resorcinols. III. Extension of the reaction between *m*-dinitrobenzene, potassium cyanide, and methanol to other alcohols. Mechanism of the reaction. A. Russell and L. M. Addison (*J. Amer. Chem. Soc.*, 1943, **65**, 2379—2380; cf. A., 1942, II, 308).—*m*-$C_6H_4(NO_2)_2$ and ROH–KCN give 2 : 6 : 1-$OR{\cdot}C_6H_3(NO_2){\cdot}CN$ (*A*), which with R'OH–KCN gives 2 : 6 : 1-$OR{\cdot}C_6H_3(OR'){\cdot}CN$ (*B*). Thus are obtained (*A*) in which R = Me (11%), m.p. 172°, Et (9%), m.p. 136°, Pr^α (3·5%), m.p. 109°, *Pr*^{β}

(7·5%), m.p. 102°, *Bu*$^{\alpha}$ (5·5%), m.p. 101°, sec.-*Bu* (4·5%), m.p. 109°, n-*amyl* (4%), m.p. 103°, and n-*hexyl* (1·5%), m.p. 88°, and (*B*) in which R = R′ = Me (85%), m.p. 118°, Et (50%), m.p. 122°, and *Pr* (6%), m.p. 45°, and R = Me, R′ = Et, m.p. 66°. The reaction mechanism is discussed. R. S. C.

Permanent fading of alkaline phenolphthalein solutions. M. H. Hubacher (*J. Amer. Chem. Soc.*, 1943, **65**, 2097—2098).—Phenolphthalein in 0·2N-NaOH in air gives a little *o*-$C_6H_4(CO_2H)_2$ (**I**) and *p*-OH·C_6H_4·CO·C_6H_4·CO_2H-*o* (39—45%), m.p. 211·1—212·9° (corr.; decomp.) [lit. 210° (decomp.)], but with 30% H_2O_2 in N-NaOH gives quinol and (**I**). *o*-Cresolphthalein, which is more stable, in 0·1N-NaOH in air gives *o*-CO_2H·C_6H_4·CO·C_6H_2Me·OH-3 : 1 : 6, m.p. 224·1—225·0° (corr.), and a trace of (**I**), and with H_2O_2 gives 2 : 1 : 4-C_6H_2Me$(OH)_2$ and (**I**). 3 : 4-Dihydroxydiphenylphthalide is less stable and in 0·1N-NaOH in air gives PhOH (43%) and (**I**) (44%). R. S. C.

Pyrolysis of 2-allyloxy-1-allyl-3-naphthoic acid. V. P. Wystrach and D. S. Tarbell (*J. Amer. Chem. Soc.*, 1943, **65**, 2472).—Adding aq. NaOH to 2 : 3-OH·$C_{10}H_4$·CO_2Me, m.p. 74—74·5°, and CH_2:CH·CH_2Br in boiling COMeEt and boiling for 6 hr. gives, after distillation in a vac., 1 : 2 : 3-CH_2:CH·CH_2·$C_{10}H_5$(OH)·CO_2Me (86·3%), b.p. 160—162°/1 mm., which by further similar treatment and then hydrolysis yields *2-allyloxy-1-allyl-3-naphthoic acid* (26%), m.p. 112·5—113°. This is unchanged at 150°, but at 214° gives 0·25 mol. of CO_2 and a tar. M.p. are corr. R. S. C.

Hydrazides of diphenic and 4-nitrodiphenic acids and their reactions. R. A. Labriola and A. Felitte (*J. Org. Chem.*, 1943, **8**, 536—539).—2-Nitrophenanthraquinone is oxidised by 6% H_2O_2 in boiling AcOH to 6-nitrodiphenic acid (**I**), m.p. 250°, in 75—80% yield. The corresponding *Me*$_2$ ester, m.p. 96°, from (**I**), MeOH, and HCl at room temp., is transformed by N_2H_4,H_2O in boiling abs. EtOH into *4-nitrodiphendihydrazide*, m.p. 209°. 4-Nitrodiphenic anhydride (**II**) and N_2H_4,H_2O yield *4-nitro-2-carboxydiphenyl-2′-carboxyhydrazide* (**III**), m.p. 200°, degraded (Curtius) to 7-nitrophenanthridone, m.p. 290° (lit. 284—285°). When heated in a vac. at 200° (**III**) gives *N-amino-4-nitrodiphenimide*, m.p. 319°. Diphenmonohydrazide is converted by diphenic anhydride in boiling EtOH into NN-*di*-o-2-*carboxyphenylbenzoylhydrazine* (**IV**), m.p. 253° (decomp.), in which N is determined by measurement of the gas evolved on treatment with 40% KOH and saturated aq. $K_3Fe(CN)_6$. (**IV**) is converted by MeOH saturated with HCl at room temp. into the *Me*$_2$ ester, m.p. 182°, hydrolysed to the original acid. (**II**) and the appropriate hydrazide in boiling EtOH afford N-o-2-*carboxyphenylbenzoyl*-N′-o-4-*nitro*-2-*carboxyphenylbenzoylhydrazine* (**V**), m.p. 261°, and N-o-2-*carboxyphenylbenzoyl*-N′-5-*nitro*-2′-*carboxyphenylbenzoylhydrazine* (**VI**), m.p. 252°; (**V**) is also obtained from (**III**) and diphenic anhydride. (**IV**), (**V**), and (**VI**) are converted by boiling Ac_2O into *compounds* considered to be oxadiazole derivatives, $C_{28}H_{16}O_4N_2$, m.p. 400°, and $C_{28}H_{15}O_6N_3$, m.p. 351° and 360°, respectively. These have no Ac and are converted by boiling KOH–EtOH into the original acids. If the Me ester is used in place of (**IV**) this change does not occur and an *Ac*$_1$ derivative, $C_{32}H_{26}O_7N_2$, m.p. 141—142°, results. H. W.

Synthesis of bis(dialkylaminoalkyl) esters of 4-fluoro*iso*phthalic acid. L. S. Fosdick and J. C. Calandra (*J. Amer Chem. Soc.*, 1943, **65**, 2308—2309).—4 : 1 : 3-$C_6H_3F(CO_2H)_2$, m.p. 282—286°, prepared from 1 : 3 : 4-$C_6H_3Me_2F$ by aq. $KMnO_4$ at 100°, with boiling $SOCl_2$ gives the *diacid dichloride*, b.p. 100—103°/2 mm., which with the appropriate NH_2-alcohol in boiling C_6H_6 gives *bis-β-di-ethyl-*, m.p. 181°, *-propyl-*, m.p. 195°, and *-butyl-aminoethyl*, m.p. 165°, and *bis-γ-di-ethyl-*, m.p. 155°, *-propyl-*, m.p. 110°, and *-butyl-amino*-n-*propyl*, m.p. 193°, 4-*fluoroisophthalate dihydrochloride*. The bases, but not the salts, are topical anæsthetics. Toxicities are one half to one eighth of that of procaine hydrochloride, increasing with the length of the side-chain. R. S. C.

Novel preparation of *s*-octahydrophenanthrene-9 : 10-dicarboxylic anhydride. C. C. Price, M. Knell, and J. P. West (*J. Amer. Chem. Soc.*, 1943, **65**, 2469—2470).—Treating 2-*cyclo*hexylidene*cyclo*hexanone (**I**) with, successively, Br and (:CH·CO)$_2$O in Et$_2$O cooled by solid CO_2–MeOH and then boiling gives *s*-octahydrophenanthrene-9 : 10-dicarboxylic anhydride (16%), m.p. 312° (block) (lit., 310°). Products from (**I**) and Br, SO_2Cl_2, or Cl_2 are unstable oils, whence no products could be isolated. (**I**) alone does not react with (:CH·CO)$_2$O. R. S. C.

Application of the conditions of the Tiemann–Reimer reaction to benzaldehyde. W. S. Rapson, D. H. Saunder, and E. T. Stewart (*J.C.S.*, 1944, 74—75).—Contrary to Chaudhuri (A., 1942, II, 227), PhCHO (0·2 mol.), $CHCl_3$ (0·2 mol.), and boiling aq. KOH (1·1 mols.) give CH_2Ph·OH (**I**), BzOH, and mandelic acid (**II**); no *o*- or *m*-$CHCl_2$·C_6H_4·CHO is obtained. PhCHO (2 mols.), $CHCl_3$ (2·2 mols.), and aq. NaOH (2 mols.) in EtOH at 100° (bath) for 30 min. afford (**I**), (**II**), BzOH, and CCl_3·CHPh·OH. A. T. P.

β-Substituted acrylacetic esters. J. English, jun., and L. J. Lapides (*J. Amer. Chem. Soc.*, 1943, **65**, 2466—2467).—CHR:CH·CO_2H and boiling $SOCl_2$ give 82—97% of CHR:CH·COCl, but PCl_5–C_6H_6 is preferable when R = 1-$C_{10}H_7$. Adding CHR:CH·COCl to freshly prepared CHAcNa·CO_2Et in xylene and keeping at room temp. for 24 hr. gives Et β-keto-α-acetyl-δ-phenyl- (75%), m.p. 46°, -2-furyl- (45%), m.p. 48°, -1-*naphthyl-* (**I**) (42%), m.p. 80°, -p-*anisyl-* (80%), m.p. 65°, -*cyclohexyl-* (**II**) (45%), and -3 : 4-methylenedioxyphenyl- (55%), m.p. 104°, -Δ$^{\gamma}$-pentenoate. Saturating these esters in N-NaOH with NH_3 at 0° and keeping at room temp. for 1 hr. gives Et β-keto-δ-phenyl- (**III**) (82%), m.p. 45—46°, -2-*furyl-* (64%), m.p. 60°, -p-*anisyl-* (70%), m.p. 44—45°, and -3 : 4-methylenedioxyphenyl- (64%), m.p. 60°, -Δ$^{\gamma}$-pentenoate, which, except for (**III**), are purified by way of their Cu salts. The reaction with NH_3 fails for (**I**) and (**II**). R. S. C.

Poly*iso*propylbenzenes. V. Acetylation. A. Newton (*J. Amer. Chem. Soc.*, 1943, **65**, 2444—2445).—With Ac_2O–$AlCl_3$ in CS_2 at 30—40°, *m*-$C_6H_4Pr^{\beta}_2$ gives *p*-$C_6H_4Pr^{\beta}$·COMe (**I**) (11·5%) (oxime, new m.p. 71·1—71·6°), 2 : 4-*di-* (**II**) (54·0%) (*semicarbazone*, m.p. 195·7—196·5°), and 2 : 4 : 6-*tri*-iso*propylacetophenone* (**III**) (11·5%), m.p. 86·6—87·1°, and (?) cumene (0·8%). *p*-$C_6H_4Pr^{\beta}_2$ gives (**I**) (15·5%), (**II**) (51·9%), (**III**) (17·1%), and cumene (2·4%). *s*-$C_6H_3Pr^{\beta}_3$ gives (**II**) (24·9%) and (**III**) (29·4%); 1 : 2 : 4 : 5-$C_6H_2Pr^{\beta}_4$ gives (**II**) (30·2%) and (**III**) (17·5%); the Pr^{β}_3 and Pr^{β}_4 compounds give also ~50% of a jelly and probably traces of (**I**) and cumene. Structures are established as follows. $KMnO_4$ oxidises (**II**) in aq. KOH at 35—37° to 2 : 4-*diisopropylphenylglyoxylic acid*, m.p. 140·1—140·8°, and 2 : 4 : 1-$C_6H_3Pr^{\beta}_2$·CO_2H, m.p. 108·7—109·5°, and (**III**) to 2 : 4 : 6-*triisopropylphenylglyoxylic acid*, m.p. variable, 195° to 207° (gas), decomp. when heated from 170° to 229° to 2 : 4 : 6 : 1-$C_6H_2Pr^{\beta}_3$·CO_2H. R. S. C.

Volatile vegetable compounds. XXVII. Presence of 2 : 4 : 4-trimethyl*cyclo*pentanone in oil of pennyroyal (*Mentha pulegium*, L.). Y. R. Naves (*Helv. Chim. Acta*, 1944, **27**, 51—56; cf. A., 1944, II, 31).—Treatment of a fraction of terpenes and alcohols, b.p. 155—162°, of the oil with Girard's reagent *P* leads to the isolation of a small proportion of 2 : 4 : 4-trimethyl*cyclo*pentanone (**I**), b.p. 159·5—160·5°/760 mm. (semicarbazone, m.p. 158·5—159°; 2 : 4-*dinitrophenylhydrazone*, m.p. 160·5—161°). It is oxidised by aq. $KMnO_4$ at room temp. to CH_2Ac·CMe_2·CH_2·CO_2H (*semicarbazone*, m.p. 170·5—171°; 2 : 4-*dinitrophenylhydrazone*, m.p. 154—154·5°) and by HNO_3 to CO_2H·CMe_2·CH_2·CHMe·CO_2H and CO_2H·CMe_2·CH_2·CO_2H. Wallach's prep. (A., 1918, i, 442) of (**I**) from 3 : 3 : 5-trimethyl*cyclo*hexanone is repeated. Temp. are corr.

Rearrangement of camphorquinone. Formation and reactions of inactive 2 : 2 : 3-trimethyl*cyclo*hexan-4-one-1-carboxylic acid.—See A., 1944, II, 107.

Structure of pyrethrolone and related compounds. I. T. F. West (*J.C.S.*, 1944, 51—53).—Pyrethrolone, prepared by treating its semicarbazone, m.p. 208°, with cold, aq. $KHSO_4$–Et_2O–CO_2, has b.p. 164—166°/2 mm. *iso*Pyrethrolone enol (**I**), b.p. 165°/1 mm., purified by fractionation or by acetylation and subsequent hydrolysis by boiling NaOMe–MeOH, has an absorption max. always at 2400 A. but ε varies from 15,000 to 27,000 (in EtOH here and below); its acetate has b.p. 143°/1·5 mm. and an absorption max. at 2300 A. (ε 18,300). Tetrahydro*iso*pyrethrolone enol (**II**), prepared from (**I**) by H_2–PtO_2–EtOAc or from tetrahydropyrethrolone (absorption max. at 2320 A.) by Zn dust in KOH–EtOH, has b.p. 155°/1 mm. and gives an acetate, b.p. 116°/1 mm. (absorption max. at 2363—2365 A., ε 12,300—20,200). Diosphenol acetate, b.p. 109°/2 mm., has an absorption max. at 2400 A. (ε 12,400). (**I**) is thus probably 2-hydroxy-3-methyl-4-Δ$^{\alpha\gamma}$-pentadienyl-Δ^{2}-*cyclo*pentenone. The absorption max. of (**II**) is displaced from 2430—2435 A. (ε 16,400—20,600) to ~2615 A. (ε 17,000) in very dil. solution (>0·005%), possibly owing to the tautomerism, 3-⟷5-methyl-4-*n*-amyl-Δ^{2}-*cyclo*penten-2-ol-1-one. R. S. C.

Polycyclic compounds. V. Reaction of chlorine with *peri*-naphthindenone. A. M. Lukin (*Bull. Acad. Sci. U.R.S.S.*, 1942, *Cl. Sci. chim.*, 55—64).—Chlorination of *peri*naphthindenone (**I**) in cold AcOH or aq. suspension yields the greenish-yellow 2-*Cl*-derivative (**II**), m.p. 152—152·5°, also obtained from (**I**) and SO_2Cl_2 in $PhNO_2$. The intermediate products are much more labile than those from bromination but can be isolated if C_6H_6 is used as solvent. Chlorination of (**I**) in C_6H_6 at 7—8° gives an orange ppt. of "*perinaphthindenone chloride*," $C_{26}H_{16}O_2Cl$ (Cl reactive to $AgNO_3$), and a solution containing colourless 2 : 3-*dichloroperinaphthindanone* (**III**) (one Cl reactive); at 40° (**III**) is formed directly. Finely powdered (**III**) when kept at 40—45° for 20 hr. is converted with some decomp. into the brownish-orange *hydrochloride* of (**II**); further heating or treatment with aq. NH_3 gives (**II**). The structure of (**II**) is confirmed by oxidation with NaOCl to naphthalic acid and by synthesis from 2 : 1-$C_{10}H_6Cl$·OH and glycerol. (**II**) is a satisfactory dye for acetate silk. Chlorination of (**I**) in AcOH at 75—80° yields a *dichloroperinaphthindenone*, m.p. 230·8—231°; if one Cl atom of this is in the probable position 2, the second cannot be in position 3 since oxidation with NaOCl yields a chloronaphthalic acid. R. C. P.

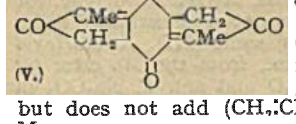
Synthesis of compounds related to the sex hormones. W. E. Bachmann, R. A. Gregg, and E. F. Pratt (*J. Amer. Chem. Soc.*,

1943, **65**, 2314—2318).—1-$C_{10}H_7$·$[CH_2]_2$·$CH(CO_2Et)_2$ (**I**) (prep. by NaOMe–EtOH–C_6H_6 in 89% yield), b.p. 170—175°/0·05 mm., in hot C_6H_6 gives a Na derivative, which with CO_2Et·$[CH_2]_2$·COCl (prep. from the H ester by $SOCl_2$ at room temp. and then the b.p.; 97% yield), b.p. 94—96°/2 mm., in C_6H_6 at 0° gives 1-$C_{10}H_7$·$[CH_2]_2$·$C(CO_2Et)_2$·CO·$[CH_2]_2$·CO_2Et (**II**), b.p. 180—195°/0·02 mm. Cyclisation of (**II**) is hindered by absence of OMe in the aromatic nucleus (cf. A., 1942, II, 263 and below). When (**II**) is cyclised by heating with 100% H_3PO_4 at 64° for 36—48 hr. and the product is hydrolysed by hot 45% aq. KOH and then decarboxylated in H_2O at 100°, there is obtained 15—23% of *β*-2-*carboxy*-(? 3 : 4-)*dihydro*-1-*phenanthrylpropionic acid* (**III**), m.p. 234—236° [Me ester (**IV**), m.p. 73—74°] (cf. Bardhan, A., 1937, II, 63). With Pd–C–N_2 at 310—320° (**IV**) gives *Me β*-2-*carbomethoxy*-1-*phenanthrylpropionate*, m.p. 114—116°, which with NaOMe in hot C_6H_6 and then hot HCl–AcOH gives 3′-keto-1 : 2-*cyclo*pentenophenanthrene, m.p. 196—197° (A., 1938, II, 17). NaOMe in boiling C_6H_6 (1 hr.) cyclises (**IV**) to 3′-*keto*-2′-*carbomethoxy*-(? 3 : 4-)*dihydro*-1 : 2-cyclo*pentenophenanthrene*, m.p. 142—144° (olive-green colour with $FeCl_3$–EtOH), whence HCl–AcOH–H_2O yields 3′-keto-(? 3 : 4)-dihydro-1 : 2-*cyclo*pentenophenanthrene (98%), m.p. 214—216° (lit., 210°, 212—213°). Hydrogenation (Pd–C) of (**IV**) in EtOAc gives *Me β*-2-*carbomethoxy*-1 : 2 : 3 : 4-*tetrahydro*-1-*phenanthrylpropionate*, m.p. 88—89°, which yields, as above, 3′-*keto*-2′-*carbomethoxy*- (91%), m.p. 134—135° (purple $FeCl_3$ colour in EtOH), and thence 3′-keto- (92%), m.p. 112—113° (Koebner *et al.*, A., 1941, II, 365, m.p. 111—112°), -1 : 2 : 3 : 4-tetrahydro-1 : 2-*cyclo*pentanophenanthrene. 6 : 1-OMe·$C_{10}H_6$·$[CH_2]_2$·$CH(CO_2Et)_2$, b.p. 193—198°/0·2 mm., gives [cf. (**II**)] the 6-OMe-derivative of (**II**), which in 100% H_3PO_4 at 42° (4—5 hr.) and then KOH gives 45% (over-all) of *β*-2 : 2-dicarboxy-7-methoxy-1 : 2 : 3 : 4-tetrahydro-1-phenanthrylidenepropionic acid, m.p. 150—151° [Me_3 ester (**V**), m.p. 159—160°]. With H_2–30% Pd–C in EtOAc and then 45% aq. KOH, (**V**) gives *β*-2 : 2-*dicarboxy*-7-*methoxy*- (93%), m.p. 193—195°, and thence (180—185°) *β*-2-carboxy-7-methoxy-1 : 2 : 3 : 4-tetrahydro-1-phenanthrylpropionic acid (95%), m.p. 150—155° [Me_2 ester (**VI**), m.p. 60—61°]. NaOMe–C_6H_6 converts (**VI**) into 3′-keto-2′-carbomethoxy-7-methoxy-, m.p. 139—141° (purple colour with $FeCl_3$–EtOH), which with HCl–AcOH–H_2O gives 7-*hydroxy*-3′-*keto*- (89%), m.p. 245—247° (vac.) (cf. Koebner *et al.*, *loc. cit.*), -1 : 2 : 3 : 4-*tetrahydro*-1 : 2-cyclo*pentanophenanthrene* (Me ether, m.p. 116—117°, b.p. 200°/0·01 mm.). The K derivative of (**I**) with CO_2Et·$[CH_2]_3$·COCl gives 1-$C_{10}H_7$·$[CH_2]_2$·$C(CO_2Et)_2$·CO·$[CH_2]_3$·CO_2Et (**VII**), a syrup, which requires 10 hr. at 100° for cyclisation by 100% H_3PO_4; subsequent boiling in conc. HCl–AcOH–N_2 gives in poor over-all yield 3-keto-1 : 2 : 3 : 4 : 5 : 6-hexahydrochrysene, m.p. 160·5—161·7° (cf. Chuang *et al.*, A., 1939, II, 270), the identity of which is confirmed by conversion (MgMeI; Pd–C) into 3-methylchrysene. The 6-OMe-derivative (prep. as above) of (**VII**) is more readily cyclised than is (**VII**); with H_3PO_4 at room temp. and then KOH–MeOH it gives *γ*-2 : 2-*dicarboxy*-7-*methoxy*-1 : 2 : 3 : 4-*tetrahydro*-1-*phenanthrylidene*-n-*butyric acid* (**VIII**), m.p. 202—203° (gas; sealed tube; preheated at 190°) (Me_3 ester, m.p. 114—115°). H_2–Pd–C reduces (**VIII**) in AcOH–EtOH to *γ*-2 : 2-*dicarboxy*-7-*methoxy*-1 : 2 : 3 : 4-*tetrahydro*-1-*phenanthryl*-n-*butyric acid*, m.p. 216—217° (gas), decarboxylated at 220° to *γ*-2-*carboxy*-7-*methoxy*-1 : 2 : 3 : 4-*tetrahydro*-1-*phenanthryl*-n-*butyric acid*, m.p. 193—194°. The Me_2 ester, m.p. 59—62°, thereof yields, as above, 3-keto-4-carbomethoxy-10-methoxy-, m.p. 167·5—168°, and 10-*hydroxy*-3-*keto*-1 : 2 : 2a : 3 : 4 : 5 : 6 : 6a-*octahydrochrysene*, m.p. 273—275° [*Me ether*, m.p. 140·5—141·5° (N_2); *benzoate*, m.p. 204—208° after softening]. R. S. C.

Carbon rings. XXXIII. Preparation of *cyclo*decane-1 : 6-dione from decahydronaphthalene. P. A. Plattner and J. Hulstkamp (*Helv. Chim. Acta*, 1944, **27**, 211—219; cf. Durland *et al.*, A., 1939, II, 156).—Undiluted, technical decahydronaphthalene is treated in countercurrent with ozonised air and the product is distilled in a vac., thus giving a fraction rich in *cis*- and *trans*-decahydronaphth-9-ols. This is converted by $ZnCl_2$ into crude $\Delta^{9:10}$-octahydronaphthalene, which is ozonised in 40% AcOH to *cyclo*decane-1 : 6-dione (**I**). The over-all yield is 14%. *trans*-1-Ketodecahydronaphthalene and δ-ketosebacic acid are among the by-products. Reduction (H_2 at 90°/50 atm.–Raney Ni–96% EtOH) of (**I**) affords a mixture (**II**), m.p. 145°, of *α*-, m.p. 151—153° (*dibenzoate*, m.p. 168°; di-*p*-nitrobenzoate, m.p. 264°), and *β*-*cyclo*decanediol, m.p. 146° (*dibenzoate*, m.p. 77°; di-*p*-nitrobenzoate, m.p. 181°). As by-product (**II**) contains *cis*-9 : 10-dihydroxydecahydronaphthalene, m.p. 89—91° (*monohydrate*, m.p. 88°), the structure of which is established by its conversion by conc. H_2SO_4 at −10° and subsequently at room temp. into *spirocyclo*pentano*cyclo*hexanone [semicarbazone, m.p. 190—193° (decomp.)]. Dehydration of (**II**) by several reagents did not yield *cyclo*decadiene; the tendency towards bridge formation appears so great that various dicyclic products result. Unsuccessful attempts to convert (**II**) into the dibromide are described. The product from (**II**) and aq. HBr appears to contain only ~20% of 6-bromo*cyclo*decanol as sole monocyclic compound; the remainder appears to consist of dicyclic Br-compounds and dicyclic alcohols. Catalytic hydrogenation (Pd–$CaCO_3$) of the crude product leads to (?) cyclo*decanol*, m.p. 62°. Small yields of (**I**) are obtained by dehydration of *cyclo*pentyl*cyclo*pentanol by $ZnCl_2$ at 150° and ozonisation of the resulting hydrocarbon in 50% AcOH and by chlorination of decahydronaphthalene at 100°, prolonged treatment of the chloride with KOH–EtOH at 100°, and ozonisation of the resulting hydrocarbon. M.p. are corr. H. W.

Ultra-violet absorption spectra of alicyclic di- and tri-ketones. H. Bastron, R. E. Davis, and L. W. Butz (*J. Org. Chem.*, 1943, **8**, 515—525).—The absorption spectra of the following have been determined in EtOH: *xxxx*-6 : 9-methano-, m.p. 75—76°, *cis*-2-methyl-, m.p. 79·6—80·6°, 5-acetoxy-2 : 7 : 8-trimethyl-, m.p. 116—117°; *xxxx*-, m.p. 123·4°, and *xyyx*-, m.p. 84·7°, -5-acetoxy-6 : 9-ethano-2-methyl-, and 2-methoxy-5-methyl-$\Delta^{2:7}$-naphthitadiene-1 : 4-dione (the configurations are assigned entirely on the basis of the Alder–Stein rule and it is uncertain which is isomeride *xxxx* and which is *xyyx*); 3-methyl*cyclo*pentane-1 : 2 : 4-trione, m.p. 118·2—119·6°, and its monohydrate, m.p. 78—80°; 5-methyl-Δ^7-naphthitene-1 : 2 : 4-trione, m.p. 174—175°; *cyclo*hexane-1 : 3-dione, m.p. 105—107°; 2-methyl*cyclo*hexane-1 : 3-dione, m.p. 205—208°; 2-*methyl*-cyclo*pentane*-1 : 3-*dione*, m.p. 212·2—214·6°; 4-hydroxy-2-methyl-*cyclo*pentane-1 : 3-dione, m.p. 165—165·8°; 5-acetoxy-2-methyl-6(or 9)-vinyl-$\Delta^{2:7}$-naphthitadiene-1 : 4-dione, m.p. 109—110°; 5-methyl-6(or 9)-vinyl-Δ^7-naphthitene-1 : 2 : 4-trione, m.p. 206—210°; 4-hydroxy-10-methyl-Δ^7-naphthitene-1 : 3-dione, m.p. 123·5°, then 145—146°; dimeride of 5-methyl*cyclo*pentene-1 : 3-dione, m.p. 213·4—215·2°. The data are applied to the elucidation of structure within this group. H. W.

Hydrogenation of 3-methyl*cyclo*pentane-1 : 2 : 4-trione. M. Orchin and L. W. Butz (*J. Amer. Chem. Soc.*, 1943, **65**, 2296—2299).—Condensing COMeEt with $Et_2C_2O_4$ by NaOEt–EtOH and boiling the product in 50% H_3PO_4 gives 3-methyl*cyclo*pentane-1 : 2 : 4-trione, (**I**) + H_2O, m.p. 74—79°, and (**II**) anhyd., m.p. 118·2—119·6°. Hydrogenation (PtO_2) of (**II**) in EtOAc gives 4-*hydroxy*-2-*methyl*cyclo*pentane*-1 : 3-*dione* (**III**) (62%), m.p. 166·6—168·2°, but of (**I**) in EtOH gives (**III**) (39%) and 2-methyl*cyclo*-pentane-1 : 3-dione (**IV**) (15%), m.p. 212—214° (Cornforth *et al.*, A., 1941, II, 19, m.p. 208—210°). A trace of H_2O favours formation of (**IV**), even in EtOAc. (**IV**) gives a violet colour with aq. $FeCl_3$ but no colour in EtOH, is a monobasic acid, with $KMnO_4$ gives $(CH_2{:}CO_2H)_2$, absorbs 2 Br in AcOH–NaOAc, has an absorption max. at 2500 A. (ε 17,800) in EtOH, and gives a *dioxime*, m.p. 198° (decomp.). (**III**) gives a colour with $FeCl_3$ in H_2O (not EtOH), is monobasic, and is unaffected by hot, dil. HCl. With CH_2N_2–Et_2O, (**III**) gives isomeric *Me ethers*, m.p. 167—168·2° and 85—86·4°, both non-acidic, giving no colour with $FeCl_3$, and hydrolysed to (**III**) by 0·05N-NaOH at 80°. With MeI–Ag_2O–MeOH at, successively, 0°, room temp., and the b.p. and then KOH–H_2O–EtOH at the b.p., (**III**) gives (?) 4-*methoxy*-2-*methyl*cyclo*pentane*-1 : 3-*dione* (small yield), m.p. 110·4—111·2° (acidic; violet $FeCl_3$ colour). H_2–PtO_2 reduces (**III**) very slowly in EtOH but no (**IV**) could be isolated. (**III**) absorbs 2 Br in AcOH–NaOAc and has an absorption max. at 2500 A. (ε 16,000). $KHSO_4$ at 160°/20 mm., later 150—155°/20 mm., converts (**III**) into (?) the *compound* (**V**), m.p. 213·4—215·2° [mol. wt. in *p*-OH·C_6H_4·O·CH_2Ph (*k* 126·15)], which is not acidic, gives no oxime, and is hydrogenated (2·34 H_2; PtO_2; EtOH) to (**IV**), but does not add $(CH_2{:}CH)_2$ in EtOH at 50° or C_6H_6 at 100°. M.p. are corr. R. S. C.


(V.)

Synthesis of condensed ring compounds. XIV. 2-Methoxy-5-methyl-$\Delta^{2:7}$-naphthitadiene-1 : 4-dione. M. Orchin and L. W. Butz (*J. Org. Chem.*, 1943, **8**, 509—514).—5-Methoxy-2-methyl-*p*-benzoquinone very slowly adds $(CH_2{:}CH)_2$ in abs. EtOH at 100° to give 2-*methoxy*-5-*methyl*-$\Delta^{2:7}$-*naphthitadiene*-1 : 4-*dione* (**I**), m.p. 94·5—95·5° (yield ~75%), converted by conc. HCl at 100° into 5-*methyl*-Δ^7-*naphthitene*-1 : 2 : 4-*trione enol*, m.p. 172—173°. Zn and MeOH–AcOH convert (**I**) into a greenish-yellow *oil*, $C_{11}H_{14}O_3$, b.p. 105—115°/0·027 mm., which does not give an enol reaction with $FeCl_3$–EtOH. (**I**) absorbs 3 H_2 (Adams' catalyst in MeOH). It is suggested as a working hypothesis that $(CH_2{:}CH)_2$ reacts faster with C atoms attached to H than to others (steric effect) and of these, as an anionoid reagent, it reacts fastest with the most cationoid C in the quinone (electrostatic effect). In some instances the rate of the favoured reaction may be so the rates of the other possible reactions that only one adduct is obtained. M.p. are corr.

[By E. W. J. Butz.] $\Delta^{1:3}$-*cyclo*Hexadiene and 1 : 2 : 5 : 6-O:$C_6H_2Me_2$:O (**II**) give (probably) 3 : 9-*dimethyl*-5 : 8-endo*ethylene*-5 : 8 : 9 : 10-*tetrahydro*-1 : 4-*naphthaquinone*, m.p. 65°, which decomposes slowly at room temp. to (**II**). H. W.

Synthesis of condensed ring compounds. XII. Preparation of a 1 : 3 : 4-triketo-9-methyl-Δ^9-octahydronaphthalene. E. W. J. Butz and L. W. Butz (*J. Org. Chem.*, 1943, **8**, 497—499; cf. A., 1943, II, 330).—5-Acetoxy-1 : 4-toluquinone (**I**) and $(CH_2{:}CH)_2$ (**II**) in EtOH at 75° for 68 hr. followed by alkaline hydrolysis give 5-*methyl*-Δ^7-*naphthitene*-1 : 2 : 4-*trione enol* (**III**), m.p. 174—175°, which gives a dark purple colour with $FeCl_3$ and titrates as a mono-

basic acid with NaOH and phenolphthalein. (III) results from the addition of (II) to the ·CMe:CH· linking of (I). The neutral by-products from (III) are oxidised by $FeCl_3$ to (?) 2-methyl-5 : 8-dihydro-1 : 4-naphthaquinone, m.p. 82—84°. On another occasion 2-methyl-1 : 4-naphthaquinone, m.p. 100—102°, was isolated, proving that some addition of (II) to the OAc·C:CH· linking of (I) has also occurred. Reduction of (III) by Zn dust and AcOH at 15° affords *4-hydroxy-10-methyl-Δ²-naphthitene-1 : 3-dione*, m.p. 130° and 146—148°, which gives a faint pink colour with $FeCl_3$. Catalytic hydrogenation (Adams) of (III) gives a H_8-compound, m.p. 180—182°, probably one of the 5-methylnaphthitane-1 : 2 : 4-triols. M.p. are corr. H. W.

Theoretical discussion, based on resonance theory, of the function of halogen in the 2-halogenobenzoquinones, the 3-halogenobenzoquinone-4-oximes, the m.p. rule for nitroso-quinonoid isomerides, and the nitration of 3-fluoroanisole and of 3-fluoro-2 : 4 : 6-trichloroanisole. H. H. Hodgson (*J. Soc. Dyers and Col.*, 1944, **60**, 65—67).—The m.p. order and variation of colour of the 2-halogenobenzoquinones are interpreted on resonance theory, which also accounts for m.p. irregularity in the 3-halogenobenzoquinone-4-oximes. Benzoquinonemonoximes and their ethers melt at a higher temp. than the tautomeric nitrosophenols, owing to predominance of a more highly polarised resonance structure. The nitrations of *m*-C_6H_4F·OMe and 3 : 2 : 4 : 6 : 1-C_6HFCl_3·OMe (all 3 Cl are replaced by NO_2 in the probable order 6, 2, 4) are also discussed. A. T. P.

Synthesis of condensed ring compounds. XIII. Preparation of 5- and 6-carbalkoxy-1 : 4-toluquinones. Addition of 5- and 6-carbomethoxy-1 : 4-toluquinone to butadiene. W. Nudenberg, A. M. Gaddis, and L. W. Butz (*J. Org. Chem.*, 1943, **8**, 500—508).—Under the experimental conditions employed, $(CH_2{:}CH)_2$ reacts only at the double linking with the ester group in 5- (I) and 6- (II) *-carbomethoxy-1 : 4-toluquinone*. 3-Methylgentisic acid (III), m.p. 219—222° (lit. 215°), obtained from 2 : 3 : 1-OH·C_6H_3Me·CO$_2$H by oxidation with $K_2S_2O_8$–NaOH followed by hydrolysis with conc. HCl at 100°, is converted into the *Me* ester, m.p. 106·6—108·2°, which is oxidised by Ag_2O–Na_2CO_3 in dry C_6H_6 at 40—50° to (II), m.p. 50·2—51·4°. This may be kept in N_2 over P_2O_5 in the dark. 4-Methylgentisic acid is converted by MeOH–HCl into a small proportion of unidentified material, m.p. 79—81°, and Me 4-methylgentisate, m.p. 119—122°, oxidised (Ag_2O–Na_2CO_3 in dry C_6H_6) to (I), m.p. 38·4—39·4°. (I) with $(CH_2{:}CH)_2$ in C_6H_6 under anhyd. conditions at 100° gives *Me 1 : 4-diketo-2-methyl-Δ²·⁷-naphthitadiene-5-carboxylate* (IV), b.p. 137—139°/0·5 mm., hydrolysed by KOH under N_2 at room temp. to 2-methyl-5 : 8-dihydronaphthalene-1 : 4-diol (V), m.p. 173—174° (and its oxidation products), and some acidic material, m.p. 110—135°, converted by $Na_2S_2O_4$ in Et_2O into (?) *o-pyruvylacetophenone* (VI), m.p. 171·4—172°, softens at 169·8°. (II) and $(CH_2{:}CH)_2$ in anhyd. C_6H_6 at 100° for 66 hr. afford *Me 1 : 4-diketo-2-methyl-Δ²·⁷-naphthitadiene-10-carboxylate* (VII), b.p. 155—157°/1—2 mm., which absorbs 3 H_2 (Adams catalyst) and is converted by alkali into (V), the identity of which is further confirmed by its oxidation to 2-methyl-5 : 8-dihydro-1 : 4-naphthaquinone; (VI) is probably isolable. In abs. MeOH at 75°/vac. for 88 hr. (II) and $(CH_2{:}CH)_2$ yield a small amount of unexamined solid, m.p. >340°, (VII), and (after hydrolysis) some (III). cyclo*Hexyl 3-methylgentisate*, b.p. 170—174°/0·25 mm., from the Me ester by alkyl exchange, is treated with dry Ag_2O and anhyd. Na_2CO_3 in C_6H_6 at 50° and the (non-isolated) quinone is transformed by $(CH_2{:}CH)_2$ at 50° into cyclo*hexyl 1 : 4-diketo-2-methyl-Δ²·⁷-naphthitadiene-10-carboxylate*, b.p. 160—161°/0·28 mm., which gives the same products as (IV) and (VII) when treated with alkali. M.p. are corr. H. W.

Syntheses in the naphthalene series. II. 3-Hydroxy-2-alkyl-1 : 4-naphthaquinones. G. Soliman and (in part) A. Latif (*J.C.S.*, 1944, 55—56).—1 : 3-$C_{10}H_6(OH)_2$ in ~3·75% EtOH–KOH (exposed to air for 2 days, followed by acidification) gives 1 : 2 : 4-O:$C_{10}H_5$(OH):O. Similarly prepared are 3-hydroxy-2-alkyl-1 : 4-naphthaquinones : alk. = Me, m.p. 174°, Et, m.p. 141°, Pr$^\alpha$, m.p. 103—104°, Pr$^\beta$, m.p. 95°, Bu$^\alpha$, m.p. 101—102°, Bu$^\beta$, m.p. 134°, and *iso*amyl, m.p. 94° [Zn–Ac_2O affords the quinol triacetate, m.p. 120° (lit. 110—112°)]; the 2-Ph analogue has m.p. 147°. A. T. P.

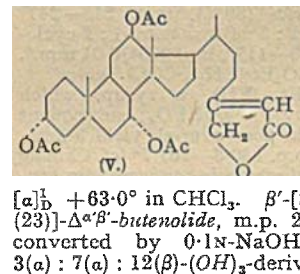
IV.—STEROLS AND STEROID SAPOGENINS.

Steroids. XXXV. Preparation of saccharide derivatives of steroids. —See A., 1944, II, 123.

Organ extracts. V. Two steroids with odour of musk from extract of swine testes. V. Prelog and L. Ruzicka (*Helv. Chim. Acta*, 1944, **27**, 61—66).—Chromatography (Al_2O_3) of the $COMe_2$ extract of swine testes leads to the isolation of Δ¹⁶-androsten-3(α)-ol, m.p. 142·5—143°, $[\alpha]_D^{20}$ +13·1°±2° in $CHCl_3$ (substance *F*), and -3(β)-ol, m.p. 122·5—123° (substance *G*), which have a marked odour of musk which is shared by the partly synthetic materials. The substances show no androgenic activity in the Fussgänger test. It is uncertain whether they are present as such in the testes or are formed from other derivatives during the working up of the extracts. M.p. are corr. H. W.

Steroids and sex hormones. XC. Preparation of the two Δ¹⁶-androsten-3-ols with odour of musk and related compounds. V. Prelog, L. Ruzicka, and P. Wieland (*Helv. Chim. Acta*, 1944, **27**, 66—71).—Thermal decomp. of androstan-17(β)-ol-3-one hexahydrobenzoate at 300° in N_2 gives hexahydrobenzoic acid and *Δ¹⁶-androsten-3-one* (I), m.p. 140—141°, $[\alpha]_D^1$ +38°±1° in $CHCl_3$, which gives an intense blue colour in Kagi and Miescher's reaction. (I) is reduced (Wolff–Kishner) to Δ¹⁶-androstene, m.p. 74·5—75·5°, $[\alpha]_D^{16}$ +17·4°±2° in 96% EtOH, readily hydrogenated to androstane, m.p. 50—50·5°, $[\alpha]_D^1$ +2°±2° in $CHCl_3$. (I) is reduced by $Al(OPr^\beta)_3$ in $Pr^\beta OH$ to *Δ¹⁶-androsten-3(α)-ol* (II), m.p. 143·5—144°, $[\alpha]_D^{16}$ +13·9°±2° in $CHCl_3$, and -3(β)-*ol* (III), m.p. 125—127°, $[\alpha]_D^{17}$ +11·2°±2·5° in $CHCl_3$ (digitonide). These are identical with substances *F* and *G* from swine testes. The odour of (I) is more intense than that of the alcohols. Reduction (H_2, PtO_2, AcOH) of (II) and (III) gives *androstan-3(α)-ol*, m.p. 145—146°, $[\alpha]_D^{17}$ +2°±2° in $CHCl_3$, and -3(β)-*ol*, m.p. 147·5—148°, $[\alpha]_D^{17}$ +0·9°±0·9° in $CHCl_3$, respectively. M.p. are corr. (Cf. preceding abstract.) H. W.

Steroids and sex hormones. XCI. β′-[3(α) : 7(α) : 12(β)-Trihydroxynorcholanyl-(23)]-Δ$^{\alpha'\beta'}$-butenolide, a homologue of the digitaloid aglucone. L. Ruzicka, P. A. Plattner, and H. Heusser [and, in part, W. Schlegel] (*Helv. Chim. Acta*, 1944, **27**, 186—194).—Triformylcholic acid, m.p. 210—211°, $[\alpha]_D^{21}$ +83·6° in $CHCl_3$ (prep. from cholic acid and 95% HCO_2H described), is converted by $SOCl_2$ in boiling abs. C_6H_6 into the chloride, which with CH_2N_2 in abs. Et_2O–C_6H_6 at −10° and subsequently at room temp. affords *25-diazo-24-keto-3(α) : 7(α) : 12(β)-triformoxy-25-homocholane* (I), m.p. 128—129° (decomp.), $[\alpha]_D^1$ −87·2° in $CHCl_3$, hydrolysed by KOH–MeOH to the (*OH*)$_3$-derivative (II), which could not be caused to crystallise. Crude (II) is transformed by glacial AcOH at room temp. and then at 95° followed by treatment with Ac_2O and C_5H_5N at 160° into *24-keto-3(α) : 7(α) : 12(β) : 25-tetra-acetoxy-25-homocholane* (III), m.p. 132—132·5°, $[\alpha]_D^{17}$ +77·1°±3° in $CHCl_3$. (I) and AcOH at 100° give *24-keto-3(α) : 7(α) : 12(β)-triformoxy-25-acetoxy-25-homocholane* (IV), m.p. 118—119°, $[\alpha]_D$ +77·5° in $CHCl_3$. $CH_2Br{\cdot}CO_2Et$, activated Zn filings, and (III) in C_6H_6–dioxan afford *β′-[3(α) : 7(α) : 12(β)-triacetoxynorcholanyl-(23)]-Δ$^{\alpha'\beta'}$-butenolide* (V), amorphous, m.p. 85—90°, $[\alpha]_D^{17}$ +74·0°±2° in $CHCl_3$, which is hydrolysed by 2N-HCl in aq. dioxan at 100° to the *β′-3(α)-hydroxy-7(α) : 12(β)-diacetoxy-*compound (VI), m.p. 162·5—163·5°, $[\alpha]_D^1$ +63·0° in $CHCl_3$. *β′-[3(α) : 7(α) : 12(β)-Triformoxynorcholanyl-(23)]-Δ$^{\alpha'\beta'}$-butenolide*, m.p. 227—228·5°, $[\alpha]_D^{17}$ +75·16° in $CHCl_3$, is converted by 0·1N-NaOH in aq. dioxan at 95° into the 3(α) : 7(α) : 12(β)-(*OH*)$_3$-derivative, m.p. 190—190·5°, $[\alpha]_D^{16}$ +23·14° in $CHCl_3$, which is transformed by Ac_2O containing a little C_5H_5N at 160° followed by hydrolysis with HCl into (VI). The crude product from the action of (IV), Zn, and $CH_2Br{\cdot}CO_2Et$ is converted by HCl in aq. EtOH into *β′-[3(α)-hydroxy-7(α) : 12(β)-diformoxynorcholanyl-(23)]-β′-hydroxybutanolide*, m.p. 232—233°, $[\alpha]_D^{17}$ +69·5° in 96% EtOH, which is transformed into the 3(α) : 7(α) : 12(β)-(*OH*)$_3$-compound, m.p. 233—234°, $[\alpha]_D^{18}$ +34·8° in 96% EtOH. M.p. are corr. (vac.). H. W.

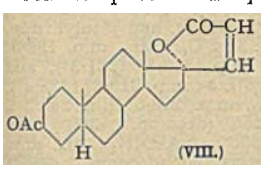


(V.)

Zimmermann reaction. Factors affecting the colour intensity; relation of molecular structure to colour production.—See C., 1944, Part 2.

Constituents of the adrenal cortex and related substances. LXVI. Reactions of androstan-3(β)-ol-17-one with propargyl alcohol and further transformations of the acetylene derivative so formed. V. Wenner and T. Reichstein (*Helv. Chim. Acta*, 1944, **27**, 24—42; cf. Ruzicka *et al.*, A., 1938, II, 99; Stavely, A., 1939, II, 119).—Δ⁵-Androsten-3(β)-ol-17-one acetate when hydrogenated (PtO_2 in AcOH), re-oxidised (CrO_3), and hydrolysed (K_2CO_3 in hot aq. MeOH) gives androstan-3(β)-ol-17-one (I), m.p. 177—179°, the mother-liquors from which after acetylation (Ac_2O in C_5H_5N at room temp.) afford ætiocholan-3(β)-ol-17-one acetate, m.p. 156—158°. (I) is transformed by $CH_2{:}C{\cdot}CH_2{\cdot}OH$ and $CMe_2Et{\cdot}OK$ at room temp. and then at 60—70° into allo*homo*-Δ²⁰-*ω-pregnine*-3(β) : 17(α) : 22-*triol* (II), leaflets, m.p. 250—251°, or needles which pass at 240—250° into leaflets, m.p. 250—251°, $[\alpha]_D^{12}$ −42·0°±3° in MeOH, converted by Ac_2O–C_5H_5N at room temp. into the 3 : 22-*diacetate* (III), tetrahedra, m.p. 134—135°, or sometimes needles, m.p. 120—125° and, after solidification, 134—135°, $[\alpha]_D^{15}$ −44·8°+2° in $COMe_2$. The configuration at $C_{(17)}$ is established by ozonisation of (III), which gives large amounts of neutral substances and an acid which is converted after alkaline hydrolysis by esterification (CH_2N_2) into Me 3(β)-17(α)-dihydroxyætio*allo*cholanate, m.p. 212—213°. Hydrogenation of (II) proceeds rapidly and, if interrupted after absorption of 1 H_2, leads to allo*homo*-Δ²⁰-*ω-pregnene*-3(β) : 17(α) : 22-*triol*, m.p. 222—224°, $[\alpha]_D^{13}$ +16·7°±3° in MeOH [3 : 22-*diacetate* (IV), m.p. 114—116°, $[\alpha]_D^{13}$ +23·6°±1·5° in $COMe_2$,

which does not give a yellow colour with $C(NO_2)_4$ but decolorises Br in $CHCl_3$]. Similar partial hydrogenation of (**III**) affords (**IV**), 17(α) : 22-*oxido*allo*homo*-Δ^{20}-ω-*pregnen*-3(β)-*ol acetate* (**V**), m.p. 152—154°, $[\alpha]_D^1$ +30·4°±1° in $COMe_2$ (hydrolysed by alkali to the free *alcohol*, needles, m.p. 186—188°, or plates which pass into these needles when heated, $[\alpha]_D^{14}$ +35·8°±2° in $COMe_2$), and a *diacetate* (**VI**), m.p. 100—102°, $[\alpha]_D^0$ +8·1°±1° in $COMe_2$. Purification is effected by protracted chromatography over Al_2O_3, which appears to cause partial conversion of (**IV**) into (**V**) and (**VI**). (**IV**) and (**VI**) appear to be *cis–trans*-isomerides since either is hydrogenated to allo*homo*-ω-*pregnane*-3(β) : 17(α)-*diol* 3-*monoacetate*, m.p. 124—125°, $[\alpha]_D^{16}$ −6·2°±2° in $COMe_2$ (obtained also from 17-allylandrostane-3(β) : 17(α)-diol 3-monoacetate), and (?) allo*homo*-ω-*pregnane*-3(β) : 17(α) : 22-*triol* 3 : 22-*diacetate*, m.p. 102—104°, and, after resolidification, m.p. 114—116°, $[\alpha]_D^1$ −5·2°±2° in $COMe_2$. Hydrogenation of (**V**) yields 17(α) : 22-*oxido*allo*homo*-ω-*pregnan*-3(β)-*ol acetate* (**VII**), m.p. 124—125°, $[\alpha]_D$ −30·0°±2° in $COMe_2$. Short ozonisation of (**V**) followed by oxidation with CrO_3 in AcOH gives neutral products, which after hydrolysis yield (**I**) and acidic substances which afford Me 3(β) : 17(α)-dihydroxyætio*allo*cholanate, m.p. 210°. (**V**) is almost quantitatively oxidised by CrO_3 in AcOH at room temp. to allo-Δ^{20}-*pregnene*-3(β) : 17(α)-*diol*-21-*carboxylactone acetate* (**VIII**), m.p. 212—214°, $[\alpha]_D^{19}$ +69·3°±2° in $COMe_2$, which reacts with 2 mols. of boiling alkali, does not give a yellow colour with $C(NO_2)_4$, and has the absorption spectrum characteristic of αβ-unsaturated lactones. It is hydrogenated to allo*pregnane*-3(β) : 17(α)-*diol*-21-*carboxylactone acetate*, m.p. 162—163°, $[\alpha]_D^{19}$ −20·9°±2° in $COMe_2$, also obtained in poor yield by oxidation of (**VII**). Hydroxylation (OsO_4 is abs. Et_2O at room temp.) of (**IV**) and (**VI**) leads to allo*homo*-ω-*pregnane*-3(β) : 17(α) : 20 : 21 : 22-*pentaols*, m.p. 260—266° [:*CMe*$_2$ *ether*, m.p. (indef.) 125—130° (decomp.)], m.p. 250—253°, $[\alpha]_D^{18}$ +5·15°±2° in MeOH (:*CMe*$_2$ *ether*, m.p. 120—125° and 175—179° after resolidification, $[\alpha]_D^{13}$ −17·55°±3° in MeOH), and m.p. 238—241°, $[\alpha]_D^{13}$ +1·9°±3° in MeOH. H. W.



(VIII.)

Isomerisation of 17-hydroxy-20-ketosteroids. V. 17*a*-Methyl-*D*-homoœtiocholane and derivatives. C. W. Shoppee (*Helv. Chim. Acta*, 1944, **27**, 8—23; cf. A., 1944, II, 51).—Successive additions of C_2H_2 and $CMe_2Et{\cdot}OK$ in $CMe_2Et{\cdot}OH$ to 3(β)-hydroxyætiocholan-17-one in C_6H_6–Et_2O give a non-cryst. product, transformed by Ac_2O–C_5H_5N at 20° into 17(α)-*hydroxy*-3(β)-*acetoxy*-Δ^{20}-*pregnine* (**I**), m.p. 140—140·5°, $[\alpha]_{5770-5790}^{15}$ −20°±1° in $COMe_2$, hydrolysed by K_2CO_3 in boiling aq. MeOH to 3(β) : 17(α)-*dihydroxy*-Δ^{20}-*pregnine*, cubes, m.p. 120—130°, rearranging to needles, m.p. 154°. (**I**) is converted by NH_2Ph in C_6H_6 and aq. $HgCl_2$ at 60° into 17(α)-*hydroxy*-3(β)-*acetoxypregnan*-20-*one*, m.p. 154°, 17a(β)-*hydroxy*-3(β)-*acetoxy*-17a-*methyl*-D-*homoœtiocholan*-17-*one* (**II**), m.p. 167°, $[\alpha]_D^{18}$ −16·5°±2° in $COMe_2$, and 17a-*anilino*-3(β)-*acetoxy*-17a-*methyl*-D-*homoœtiocholan*-17-*one*, m.p. 184—185°, $[\alpha]_D^{18}$ −62°±2° in $COMe_2$ [corresponding *nitrosoamine*, m.p. 192—194° (decomp.)]. (**II**) is unchanged by contact with Al_2O_3 in moist C_6H_6, is converted by boiling KOH–MeOH into 3(β) : 17a(β)-*dihydroxy*-17a-*methyl*-D-*homoœtiocholan*-17-*one* (**III**), m.p. 202—203° (becomes opaque at ~130°), and by Ac_2O and BF_3,Et_2O in AcOH at 20° into the *diacetate* (**IV**), m.p. 202—204°, $[\alpha]_D^{13}$ +8°±2° in $COMe_2$, of (**III**). (**I**) is converted by HgO and BF_3,Et_2O in AcOH containing Ac_2O at 20° into (**IV**) (also isolated in platelets, m.p. 220—222°), and 3(β) : 17(α)-*diacetoxypregnan*-20-*one*, m.p. 170—171°, transformed by boiling KOH–MeOH into 3(β) : 17a(α)-*dihydroxy*-17a-*methyl*-D-*homoœtiocholan*-17-*one*, m.p. 212° (becomes opaque at ~80°), which yields (Ac_2O in C_5H_5N at 20°) the 3(β)-*acetoxy*- (**V**), m.p. 180—183°, $[\alpha]_D$ −17°±2° in $COMe_2$, and thence (Ac_2O–BF_3,Et_2O in AcOH at 20°) the 3(β) : 17a(α)-*diacetoxy*-, m.p. 222°, -compound. Successive treatments of (**V**) with PBr_3 in C_6H_6 and Zn dust–AcOH lead to 3(β)-*acetoxy*-17a-*methyl*-D-*homoœtiocholan*-17-*one*, m.p. 110—112°, $[\alpha]_D^{20}$ −33°±3° in $COMe_2$, hydrolysed to the 3(β)-*OH*-compound, m.p. 214—218°, which is oxidised (CrO_3 in AcOH) to 17a-*methyl*-D-*homoœtiocholane*-3 : 17-*dione*, prisms, m.p. 132°, resolidifying to needles, m.p. 146—148°, $[\alpha]_D^{20}$ −36·5°±2° in $COMe_2$; this is transformed by N_2H_4,H_2O and NaOEt–EtOH at 175° into 17a-*methyl*-D-*homoœtiocholane*, m.p. 86—88°, $[\alpha]_D^7$ 0°±2°, $[\alpha]_{5461}$ +1·7°±2° in $COMe_2$, $[\alpha]_D^{17}$ 0°±2·5°, $[\alpha]_{5460}^{17}$ +1·7°±2·5° in dioxan. (**V**) and N_2H_4,H_2O in NaOEt–EtOH at 175° yield 3(β)-*hydroxy*-17a-*methyl*-D-*homo*-Δ^{17}-*œtiocholene*, prisms, m.p. 135°, which pass into long needles, m.p. 162°, $[\alpha]_D^{14}$ +62°±2·5° in $COMe_2$, hydrogenated (PtO_2 in AcOH at 20°) to 3(β)-*hydroxy*-17a-*methyl*-D-*homoœtiocholane*, m.p. 183—184°, $[\alpha]_D^{14}$ 0°±3° in $COMe_2$, which is oxidised (CrO_3 in AcOH at 20°) to 17a-*methyl*-D-*homoœtiocholan*-3-*one* (**VI**), m.p. 116—117°, $[\alpha]_D^{12}$ +17°±2° in $COMe_2$. (**VI**) is transformed by Br–AcOH followed by boiling C_5H_5N into 17*a*-methyl-*D*-homo-Δ^4-ætiocholen-3-one, m.p. 132—134°, reduced to 17*a*-methyl-*D*-homoandrostan-3-one (**VII**), m.p. 180°. Hydrogenation and subsequent oxidation of 17*a*-methyl-*D*-homo-Δ$^{4:17}$-androstadien-3-one affords (**VI**) and (**VII**). M.p. are corr. (block). Limit of error ±2°. H. W.

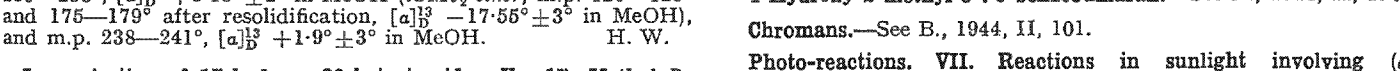
V.—TERPENES AND TRITERPENOID SAPOGENINS.

Diterpenes. Synthesis of 3 : 6-dimethyl-1-*iso*propylacenaphthene and of 1 : 5-dimethyl-2-naphthol.—See A., 1944, II, 124.

Synthesis of tricyclenone. S. S. Nametkin and A. S. Zabrodina (*Compt. rend. Acad. Sci. U.R.S.S.*, 1942, **36**, 142—144).—Bornylenol (**I**) (Nametkin *et al.*, A., 1938, II, 148) is oxidised (CrO_3 in AcOH) to *tricyclenone* (**II**), m.p. 111—112° [*semicarbazone* (**III**), m.p. 214—215°]. (**III**) is converted by NaOEt–EtOH at 160—170° into tricyclene, m.p. 62—63·5°, further identified by hydration (glacial AcOH containing a little 50% H_2SO_4) to *iso*borneol (phenylurethane, m.p. 139°). A mechanism of formation of (**II**) from (**I**) is suggested but it is also possible that (**I**) is actually tricyclenol. H. W.

VI.—HETEROCYCLIC.

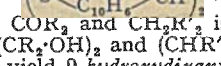
Reaction between lactones and the Grignard reagent. II. Intermediate stages of the reaction. T. A. Geissman and E. Baumgarten (*J. Amer. Chem. Soc.*, 1943, **65**, 2135—2136; cf. A., 1941, II, 201).—2 : 3-Diphenylchromen-2-ol (prep. from the 3-phenylflavylium ferrichloride by Et_2O–H_2O), m.p. 122—122·5°, with MgPhBr in Et_2O gives 2 : 3 : 4-triphenylchroman-2-ol (72%), m.p. 158·5—159°, dehydrated by H_3PO_4–AcOH to 2 : 3 : 4-triphenyl-Δ^2-chromene, m.p. 129—129·5° (lit., 131°) (cf. A., 1940, II, 313). Reaction thus proceeds by way of



o-OMgBr·C_6H_4·CHPh·CPh:CPh·OMgBr. No chromenol could be obtained from flavylium perchlorate, but 4-phenylflavylium ferrichloride in aq. $COMe_2$ gives 2 : 4-*diphenylchroman*-2-*ol*, m.p. 68—71° (immediate) or 136—138° (slow heating). With MgPhBr this gives *o*-OH·C_6H_4·CPh:CH·COPh (**I**) and 2 : 3 : 4-triphenyl-Δ^2-chromene [also obtained from (**I**) by hot AcOH]. R. S. C.

4-Hydroxy-2-methyl-5 : 6-benzcoumaran.—See A., 1944, II, 128.

Chromans.—See B., 1944, II, 101.

Photo-reactions. VII. Reactions in sunlight involving (*a*) rupture of the ethane linking, (*b*) dehydrogenation effected by quinone and benzophenone derivatives, and (*c*) addition reactions between ketones and methanes. A. Schonberg and A. Mustafa (*J.C.S.*, 1944, 67—71; cf. A., 1943, II, 265).—Reduction of $CO(C_6H_4R\text{-}p)_2$ (R = Cl or OMe) in Pr$^\beta$OH and sunlight (in 15 or 30 days, respectively) to the corresponding pinacols occurs. The reverse reaction is illustrated when xanthopinacol (**I**) or fluorenopinacol is photochemically transformed (in $COMe_2$ in 31 days) into Pr$^\beta$OH and xanthone (**II**) or fluorenone, respectively; the mechanism of the rupture of the C–C linking is discussed. Photo-oxidation of $(OH{\cdot}CPhMe)_2$ (40 days), $(OH{\cdot}CR_2)_2$ (**III**) [R = Ph (14 days), *p*-C_6H_4·OMe (31 days), *p*-C_6H_4Me (10 days), or *p*-C_6H_4Cl (20 days)], 9 : 10-dihydroxy-9 : 10-diphenyldihydrophenanthrene (**IV**) (4 days), and 7 : 8-diphenylacenaphthene glycol (**V**) (7 days) in C_6H_6 with *o*-O:C_6H_4:O (**VI**) follows the reaction: (**III**) + 2(**VI**) → $2COR_2$ + O:C_6H_4:O,$C_6H_4(OH)_2$. (**V**) or (**VI**) yields (*o*-$C_6H_4Bz)_2$ or 1 : 8-$C_{10}H_6Bz_2$, respectively. (**I**) and (**VI**) give an excellent yield of (**II**). $CPh_3{\cdot}OH$ does not react with (**VI**) in C_6H_6 in sunlight. $(C_6H_4R\text{-}p)_2CH{\cdot}OH$ (R = OMe or Me) is converted in sunlight in $COMe_2$ (1 month) into the corresponding pinacol + Pr$^\beta$OH. CH_2Ph_2 and (**VI**), after exposure for 1 month, yield quinhydrone and $(CHPh_2)_2$. Similarly, fluorene, xanthen (**VII**), anthrone, and dinaphthapyran afford difluorenyl, dixanthyl (**VIII**), dianthrone (**IX**), and bisdinaphthaxanthen  , respectively. Photochemical action between COR_2 and $CH_2R'_2$ is either additive ($OH{\cdot}CR_2{\cdot}CHR'_2$) or affords $(CR_2{\cdot}OH)_2$ and $(CHR'_2)_2$. Thus (**VII**) and (**II**) in a few hr. in C_6H_6 yield 9-*hydroxydixanthyl*, m.p. 194° (decomp.) (dehydrated by AcCl to dixanthylene), and (**VII**) and $COPh_2$ (10 days) yield *diphenyl*-9-*xanthylcarbinol*, m.p. 160° (dehydrated to *oo'*-oxidotetraphenylethylene). $(CHPh_2)_2$ is formed from CH_2Ph_2 and anthraquinone (5 months) or (**II**) (3 months); (**II**) and anthrone (1 month) give (**IX**). Dinaphthapyran and (**II**) (10 days in C_6H_6) give *bisdinaphthaxanthen*, m.p. >300°. None of the reactions proceeds in the dark. Another type of reaction is illustrated: (**VII**) and COPhMe or $CO(C_6H_4R\text{-}p)_2$ (R = OMe or Cl) give (**VIII**) and the corresponding pinacol. Thioketones show greater resistance than the corresponding ketones. Thus, $CS(C_6H_4R\text{-}p)_2$ (R = OMe or NMe_2), xanthione, thioxanthione, *N*-phenylthioacridone, 2 : 6-diphenyldithiopyrone, and 4-thioflavone do not react in Pr$^\beta$OH in sunlight for 7 days. Also, CH_2Ph_2 does not react with $CS(C_6H_4{\cdot}OMe\text{-}p)_2$. A. T. P.

Synthesis of a second isomeric form of 3 : 4-diaminotetrahydrothiophen. G. W. Kilmer and H. McKennis (*J. Biol. Chem.*, 1944, **152**, 103—111).—(:CH·CH_2·OAc)$_2$ and Br in $CHCl_3$ at −30° to −40° give $(CHBr{\cdot}CH_2{\cdot}OAc)_2$ (**I**), m.p. 84—85°, which with HCl–MeOH at 45—47° affords $(CHBr{\cdot}CH_2{\cdot}OH)_2$, m.p. 131—131·5°. This is converted by *o*-$C_6H_4(CO)_2NK$ in xylene at 170° into *βγ-diphthalimidobutane-αδ-diol* (**II**), m.p. 300—302°, slowly hydrolysed by

boiling 48% HBr to *βγ-diaminobutane-αδ-diol dihydrobromide* (**III**), incipient decomp. ~220°, which gives a *Bz*$_2$ derivative (**IV**), m.p. 208—209° (*dibenzoate*, m.p. 203—204°). (**III**) is less advantageously obtained by converting (**I**) by *o*-$C_6H_4(CO)_2NK$ in boiling xylene into *βγ-diphthalimido-αδ-diacetoxybutane*, m.p. 250°, transformed by boiling 48% HBr into (**III**) with some (?) *β-bromo-γ-phthalimido-αδ-diacetoxybutane*, m.p. 148—149°. Attempts to replace the OH groups of (**II**) by halogen by use of $SOCl_2$, PCl_5, or P + I were unpromising and the prep. of an αδ-dihalogenobutane derivative from (**III**), (**IV**), or *βγ-di*-p-*bromobenzenesulphonamidobutane-αδ-diol*, m.p. 245—247°, by a variety of reagents was unsatisfactory. (**III**) does not react with PCl_5 in presence of AcCl and is largely unchanged by boiling 57% HI. (**III**) is converted by aq. Ag_2SO_4 followed by conc. H_2SO_4 at 140° into *βγ-diamino-αδ-butyl* H_2 *disulphate*, decomp. >280°, which with aq. Na_2S at 140° yields 3 : 4-diaminotetrahydrothiophen (isomeride *B*) (**V**) (*Bz*$_2$, m.p. 238—239°, and *Ac*$_2$ derivative, m.p. 173—175° or, after crystallisation from $COMe_2$, m.p. 135—141°) isolated as the *dipicrate* (**VI**), incipient decomp. 220°. (**VI**) is converted into the dihydrochloride, which when heated with 85% H_3PO_4 at 400° and then treated with Br in CCl_4 affords tetrabromothiophen. (**V**) differs from isomeride *A* (A., 1943, II, 44) in its derivatives and by its failure to yield a dibenzquinoxaline derivative. It resembles *A* in its inability to give a cyclic carbamide under the conditions which lead to the resynthesis of biotin from 3 : 4-diamino-2-tetrahydrothiophen-*n*-valeric acid.

H. W.

Synthesis of 3-phenylpiperidines. C. F. Koelsch (*J. Amer. Chem. Soc.*, 1943, **65**, 2093—2095).—Hydrogenation (Raney Ni; 150°/200 atm.; EtOH) of CN·CHPh·$[CH_2]_2$·CO_2Me gives *5-phenyl-2-piperidone* (88%), m.p. 127—129°, without formation of *sec.* bases. Na–Bu$^{\alpha}$OH then yields 3-phenylpiperidine (57%), m.p. 14—15°, b.p. 139—142°/19 mm. [*Bz* derivative, m.p. 89—90°; hydrochloride, m.p. 143—144° (lit., 146—147°)]. CN·CHPh·CHMe·CH_2·CO_2Et gives similarly *5-phenyl-4-methyl-2-piperidone*, α-, m.p. 210—212°, and *β-form*, m.p. 89—92°, b.p. (both forms) 210—220°/10 mm., and thence *3-phenyl-4-methylpiperidine*, α-, m.p. 10°, b.p. 143—144°/22 mm. (*hydrochloride*, m.p. 189—190°; *Bz* derivative, m.p. 129—130°; picrate, m.p. 188—189°), and *β-form*, b.p. 151—153°/23 mm. (*hydrochloride*, m.p. 250—252°; *Bz* derivative, m.p. 100—101°; picrate, m.p. 217—218·5°). Similarly are obtained *5-phenyl-4 : 4-dimethyl-*, m.p. 167—169°, *4 : 5-diphenyl-*, α-, m.p. 192—194°, and *β-form*, sinters 174°, m.p. 177—178°, and *4-carbethoxy-5-phenyl-2-piperidone*, α-, m.p. 162—163°, b.p. 244°/9 mm., and β-form, m.p. 74—77°, 3-phenyl-4 : 4-dimethyl- (hydrochloride, m.p. 274—276°; *Bz* derivative, m.p. 108—110°), *3 : 4-diphenyl-piperidine*, α-, m.p. 83—84°, b.p. 230—240°/23 mm. [*hydrochloride*, m.p. 197—199°; *Bz*, m.p. 138—139°, and 1-*Me* derivative, m.p. 79—80°, b.p. ~195°/15 mm. (*hydrochloride*, m.p. 203—206°)], and *β-form*, m.p. 115—116° (hydrochloride, an oil; *nitrate*, m.p. 165—166°; *Bz*, m.p. 159—160°, and 1-*Me* derivative, m.p. 54—57°, b.p. 200—210°/15 mm.), and *3-phenylpiperidine-4-carboxylic* [*3-phenylisonipecotic*] *acid* (**I**), sublimes ~360° (decomp.) {*Me* ester, m.p. 62—63° [*hydrochloride*, m.p. 253—255° (decomp.)]}. (**I**) is accompanied by *3-phenyl-4-piperidylcarbinol*, sinters 98°, m.p. 110°, b.p. 215—218°/24 mm.

R. S. C.

Halogenation of pyridine. S. M. McElvain and M. A. Goese (*J. Amer. Chem. Soc.*, 1943, **65**, 2227—2233).—Passing C_5H_5N (6) and Br (9 mols.) through a packed tube (cf. C., 1944, Part 2) at 500° gives 2-bromo- (**I**) (46%) (gives no quaternary salts) and 2 : 6-dibromo-pyridine (17%) (cf. den Hertog *et al.*, A., 1932, 522). Similar prep. of 3-bromopyridine (**II**) is slow, but C_5H_5N,HCl (2 mols.) and Br (1 mol.) give a perbromide which at 160—170° evolves HCl and at 195—200° gives (apparatus : C., *loc. cit.*) (**II**) (37%) and 3 : 5-dibromopyridine (26%) (*methiodide*, m.p. 273—274°; *metho-p-toluenesulphonate*, m.p. 219—221°) (cf. A., 1929, 577). (**II**) gives a *hydrochloride*, m.p. 158—159°, *methiodide*, m.p. 164—165°, and *metho*-p-*toluenesulphonate*, m.p. 156—157°. C_5H_5N and Br give exothermally a cryst. perbromide (**III**), which at 250—260° gives black material (~50%), a fraction (*A*) (27%) containing (**II**), a small amount of 3 : 4-dibromopyridine, and ~2% of (**I**). When kept, (*A*) deposits successively salts, m.p. 165—167° (~20% of ionic Br) and ~300° (~32% of ionic Br). C_5H_5N and (**III**) at ~70° give exothermally a black salt, probably of polypyridylene type. C_5H_5N,HBr gives a perbromide which undergoes autobromination at 230—250°; the sulphate cannot be used. C_5H_5N,HCl slowly gives a semi-solid perchloride, which loses Cl at >100° and at 160—180° gives ~4% each of 3-chloro- and 3 : 5-dichloro-pyridine. C_5H_5N,HCl (1·5 mols.) and I (0·75 mol.) give a stable periodide, m.p. ~150°, which at 280—290° gives 37% of pentaiodopyridine. Methylpyridine hydrochlorides give perbromides which at >135° give black polymers, but the 2-Me derivative (**IV**) at 120—130° gives very slowly 3% of *5-bromo-2-methylpyridine*, b.p. 73—74°/17 mm. 2-Methylpyridine and (**IV**) give black polymers.

R. S. C.

Sulphonation of pyridine and picolines. S. M. McElvain and M. A. Goese (*J. Amer. Chem. Soc.*, 1943, **65**, 2233—2236).—At 220—230° 20—22% oleum with C_5H_5N gives pyridine-3-sulphonic acid (71% in 24 hr.), m.p. 352—356° (block), and with 2-, 3-, and 4-methylpyridine gives, respectively, 6- (60% in 24 hr.), darkens 318°, m.p. 338—341° (block), 5- (23% in 16 hr.), darkens 308°, m.p. 312—314° (block), and *4-methylpyridine-3-sulphonic acid* (40% in 8 hr.), darkens 310°, m.p. 353—355° (block). The Na salts of these acids with NaCN at 340—400° give nicotinonitrile (46%), m.p. 49—50°, 6- (8%), m.p. 84—85° (lit. 58°), 5- (35%), m.p. 83—84°, and 4-*methylpyridine-3-nitrile* (12%), m.p. 43—44° (and much C_5H_5N etc.), hydrolysed to the appropriate acids.

R. S. C.

Hydrolysis of nicotinonitrile by ammonia. C. F. Krewson and J. F. Couch (*J. Amer. Chem. Soc.*, 1943, **65**, 2256—2257).—Nicotinonitrile and conc. aq. NH_3 at 107—109° (bomb) give nicotinamide (72·66—98·93%) and a small amount of acid. Addition of NaOH yields more acid. H_2O_2–NH_3 gives 94—96% yields more quickly. H_2O_2–NaOH at 50° give 89—93% of less pure amide.

R. S. C.

Azo-dyes. II. Preparation and bacteriostatic properties of azo-derivatives of 8-hydroxyquinoline. R. N. Shreve and R. B. Bennett (*J. Amer. Chem. Soc.*, 1943, **65**, 2243—2245; cf. A., 1944, II, 111).—*5-Arylazo-8-hydroxyquinolines* (figures in parentheses are m.p. of the *hydrochlorides*) are prepared in which aryl = Ph, m.p. 172·4° (lit. 174°) (202°), *o*-, m.p. 211·6° (241·2°), *m*-, m.p. 192·2° (236·6°), and *p*-C_6H_4Cl, m.p. 232·8° (238·7°), 2 : 5 : 1-$C_6H_3Cl_2$, m.p. 246·8° (239·3°), *o*-, m.p. 178·1° (213·2°), *m*-, m.p. 167·8° (226·1°), and *p*-tolyl, m.p. 189·1° (lit. 185—186°) (sinters 207°), 1 : 3 : 2-$C_6H_3Me_2$, m.p. 196·5° (223·3°), *o*-, m.p. 221·1° (206·6°), *m*-, m.p. 249·4° (221·3°), and *p*-NO_2·C_6H_4, m.p. 283·5° (lit. 281°) (225·8°), *o*-, m.p. 219·2° (228·4°), *m*-, m.p. 237° (258·3°), and *p*-OH·C_6H_4, m.p. 228·5° (lit. 248·2°), *o*-, m.p. 250° (sinters 198°), *m*-, m.p. 256° (decomp. >300°), and *p*-CO_2H·C_6H_4, m.p. 287·7° (decomp. >300°), *p*-AsO_3H_2·C_6H_4, m.p. 235·4° (219·8°), *p-p'*-NH_2·C_6H_4·C_6H_4, sinters 265° (decomp. >300°), 4'-amino-3 : 3'-dimethoxydiphenylyl-4-, m.p. 285·6° (decomp. >300°), *m*- and *p*-SO_3H·C_6H_4, 1 : 4-, 1 : 2-, and 6 : 2-SO_3H·$C_{10}H_6$, and 1 : 3 : 6 : 8-OH·$C_{10}H_4(SO_3H)_2$, decomp. >300° (decomp. >300°). *4 : 4'-Bis-8''-hydroxyquinoline-5''-azodiphenyl*, decomp. >300° (decomp. >300°), is also prepared. Solubilities of the bases in 95% EtOH and of the hydrochlorides in $(CH_2·OH)_2$ and 0·1N-HCl are recorded. For bacteriostatic properties see A., 1944, III, 295.

R. S. C.

Barbiturates containing the Δ^2-*cyclo*pentenyl group. A. P. Centolella, J. W. Nelson, and H. G. Kolloff (*J. Amer. Chem. Soc.*, 1943, **65**, 2091—2092).—The following are prepared. Et_2 Δ^2-*cyclo*pentenylalkylmalonates, in which alkyl = Me, b.p. 138—142°/19 mm., Et, b.p. 141—146°/12 mm., Pr$^{\alpha}$, b.p. 158—163°/25 mm., Bu$^{\beta}$, b.p. 158—163°/7 mm., allyl, b.p. 149—155°/16 mm., *iso-*, b.p. 138—140°/7 mm., and *n*-propenyl, b.p. 146—152°/11 mm., and β-methylallyl, b.p. 157—161°/18 mm.; *5-Δ^2-cyclo*pentenyl-5-ethyl-, m.p. 160—161°, -5-*n*-propyl-, m.p. 147—148°, *-5-propenyl-*, m.p. 186—188°, *-5-allyl-* (**I**), m.p. 139—140°, -5-iso*propenyl-*, m.p. 136—137°, *-5-β-*bromoallyl-, m.p. 192—193°, *-5-β-methylallyl-*, m.p. 168—169°, and -5-iso*butyl-barbituric acid*, m.p. 171—172°; *5-Δ^2-cyclopentenyl-5-ethyl-*, m.p. 194—195°, -5-*n*-propyl-, m.p. 126—127°, *-5-allyl-*, m.p. 150—151°, -5-iso*propenyl-*, decomp. when heated, *-5-β-bromoallyl-*, m.p. 206—207°, *-5-β-methylallyl-*, m.p. 178—180°, and -5-iso*butyl-thiobarbituric acid*, m.p. 150—151°; *5-Δ^2-cyclopentenyl-1 : 5-dimethylbarbituric acid*, m.p. 138—139°; *5-Δ^2-cyclopentenyl-1-methyl-5-ethyl-*, m.p. 117—118°, -5-n-*propyl-*, m.p. 104—105°, -5-allyl-, m.p. 96—97°, -5-iso*propenyl-*, m.p. 137—139°, *-5-β-bromoallyl-*, m.p. 139—141°, *-5-β-methylallyl-*, m.p. 132—133°, and -5-iso*butyl-barbituric acid*, m.p. 150—151°. The min. effective and lethal doses, the induction period, and duration of anæsthesia of these acids are recorded. (**I**) is the most promising compound.

R. S. C.

Pyrazole compounds. V. Acylation of 3-hydroxy-1-phenyl-5-pyrazoloneimide. A. Weissberger and H. D. Porter (*J. Amer. Chem. Soc.*, 1943, **65**, 2180—2183; cf. A., 1944, II, 58).—5-Amino-3-hydroxy-1-phenyl-5-pyrazoline (**I**) in Ac_2O at 100° gives *5-imino-3-acetoxy-4-acetyl-1-phenylpyrazoline* (**II**) (25%), m.p. 192—193°, and *5-acetimido-3-hydroxy-1-phenylpyrazoline* (**III**) (14%), m.p. 233—234°. 2% NaOH at room temp. hydrolyses (**II**) to *5-imino-3-hydroxy-4-acetyl-1-phenylpyrazoline* (86%), m.p. 233—234°, which is stable in hot 10% NaOH but in Ac_2O at 100° regenerates (**II**). With C_5H_5N in Ac_2O at 100° (**I**) gives *5-acetimido-2-acetyl-3-acetoxy-1-phenyl-Δ^3-pyrazoline* (72%), m.p. 83—84°, converted slowly into (**I**) by 10% NaOH at 100° and by 2% NaOH at room temp. into (**III**). Adding BzCl to (**I**) and C_5H_5N in dioxan at 100° gives *5-imino-3-benzoyloxy-1-phenylpyrazoline* (**IV**) (35%), m.p. 105—106°, and *5-benzimido-3-benzoyloxy-1-phenylpyrazoline* (**V**) (10%), m.p. 193—194°, but an excess of BzCl and C_5H_5N yields 75% of (**V**). NaOH in aq. EtOH at room temp. hydrolyses (**V**) to *5-benzimido-3-hydroxy-1-phenylpyrazoline* (**VI**), m.p. 237—238°, or (**IV**) or (**I**); aq. NaOH converts (**V**) into (**VI**) and then into (**I**). Further benzoylation of (**IV**) or (**VI**) gives (**V**).

R. S. C.

Pyridine and pyrazole derivatives.—See B., 1944, II, 101.

Pyridylquinolines.—See B., 1944, II, 102.

Keten acetals. XII. Reaction of keten diethyl acetal with diazonium salts. S. M. McElvain and A. Jelinek (*J. Amer. Chem. Soc.*, 1943, **65**, 2236—2239; cf. A., 1943, II, 79).—PhN_2Cl (0·1l) and

$CH_2{:}C(OEt)_2$ (I) (0·5 mol.) at the b.p. give EtCl (62%), N_2 (7%), 4-ethoxy-1-phenylpyridaz-6-one, NPh<N=CH / CO·CH>C·OEt (35%), m.p. 125—126° (Sonn, A., 1935, 990, m.p. 124—125°) [hydrolysed by NaOH in boiling 75% EtOH to the OH-derivative, m.p. 229—230° (*loc. cit.*, 221—222°), EtOAc, $CMe(OEt)_3$, $CHEtAc{\cdot}CO_2Et$, and dimerides of (I). *p*-$OEt{\cdot}C_6H_4{\cdot}N_2Cl$ and (I) give di-*p*-anisylformazyl formate, *p*-$OEt{\cdot}C_6H_4{\cdot}NH{\cdot}N{:}C(CO_2Et){\cdot}N{:}N{\cdot}C_6H_4{\cdot}OEt$-*p* (27%), m.p. 130—131°, and 4-*ethoxy*-1-p-*anisylpyridaz*-6-*one* (25%), m.p. 159—160°. *p*-$NO_2{\cdot}C_6H_4{\cdot}N_2Cl$ and (I) give 4-*ethoxy*-1-p-*nitrophenylpyridaz*-6-*one* (II) (25%), m.p. 249—250°, and impure Et *p*-nitrobenzoylformate-*p*-nitrophenylhydrazone, darkens 150°, decomp. 183—185°. *p*-$CO_2Et{\cdot}C_6H_4{\cdot}N_2Cl$ and (I) give 4-*ethoxy*-1-p-*carbethoxyphenylpyridaz*-6-*one* (33%), m.p. 131—132°, and *Et glyoxylate*-p-*carbethoxyphenylhydrazone* (1·2%), m.p. 92—93°. 4-Hydroxy-3-carboxy-1-*p*-nitrophenylpyridaz-6-one (III) in Ph_2O at 250° gives CO_2 and 4-*hydroxy*-1-p-*nitrophenylpyridaz*-6-*one* (IV) (76%), m.p. 299—300°, which with 1 equiv. each of NaOEt and EtI gives (II). Hydrogenation (Raney Ni; H_2O; 50°/500 lb.) of the Na salts of (III) and (IV) gives 4-*hydroxy*-3-*carboxy*- (65%), m.p. 297—299° (gas), and 4-*hydroxy*-1-p-*aminophenylpyridaz*-6-*one* (60%), m.p. 250—251°, respectively. R. S. C.

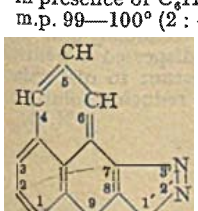
Derivatives of 4-pyrimidylacetic acid. D. E. Worrall (*J. Amer. Chem. Soc.*, 1943, **65**, 2053—2054).—2-Imino-6-keto-1 : 2 : 3 : 6-tetrahydro-4-pyrimidylacetic acid, m.p. 189—190° (decomp.), is obtained from $NH{:}C(NH_2)_2{,}H_2CO_3$ and $CO(CH_2{\cdot}CO_2Et)_2$ in boiling EtOH (cf. A., 1918, i, 409). It gives salts with mineral acids, alkalis, and NH_3. With HCl–MeOH it gives the *Me* ester, m.p. 192—193° (decomp.) (*hydrochloride*), with conc. NH_3 gives the *amide*, m.p. >285° (decomp.), with HCl–$OH{\cdot}[CH_2]_2{\cdot}Cl$ gives the $Cl{\cdot}[CH_2]_2$ ester, m.p. 164°, with boiling NaOH–MeI–EtOH gives the 1-*Me* derivative, m.p. 256—258° (decomp.), and with conc. HNO_3 gives a nitrate, which by evaporation at 100° gives a NO_3- and thence (Sn–HCl) the 5-NH_2-*acid*, m.p. indefinite (decomp.). With Br–AcOH it gives the 5-*Br-acid*, m.p. indefinite (*hydrobromide*, m.p. indefinite). R. S. C.

Preparation of octahydrophenazone. M. A. Phillips (*Chem. and Ind.*, 1944, 129).—2-Chloro*cyclo*hexanone, NH_3 (*d* 0·88), and EtOH at 100°, in a sealed tube or on a water-bath in a current of CO_2, afford octahydrophenazone, m.p. 108° (hydrochloride, m.p. 147—150°). A. T. P.

ωω′-Dimethionine.—See A., 1944, II, 122.

5-Ethyl-5-2′-pyridylbarbituric acid. S. M. McElvain and M. A. Goese (*J. Amer. Chem. Soc.*, 1943, **65**, 2226—2227).—Et_2 2-pyridylmalonate, $CO(NH_2)_2$, and NaOBu$^{\gamma}$ in boiling Bu$^{\gamma}$OH give α-2-*pyridylbutyrylcarbamide* (55%), m.p. 122—123°, and 5-2′-*pyridyl*-5-*ethylbarbituric acid* (I) (10%), m.p. 257—258° (cf. A., 1935, 1504). (I) has no hypnotic or anæsthetic action (rats). R. S. C.

Polynuclear, condensed systems with heterocyclic rings. XIV. Attempted ring-closure with 1-phenyl-1 : 2 : 3-triazole-4 : 5-dicarboxylic acid. W. Borsche, H. Hahn, and M. Wagner-Roemmich (*Annalen*, 1943, **554**, 15—23).—1-Phenyl-1 : 2 : 3-triazole-4 : 5-dicarboxylic acid (I) (Me_2 ester, m.p. 127°), obtained by the oxidation of 1-phenyl-5-methyl-1 : 2 : 3-triazole-4-carboxylic acid (II) by $KMnO_4$, is converted by $SOCl_2$ into the *dichloride*, m.p. 40° (corresponding *dianilide*, m.p. 255°); this is transformed by $AlCl_3$ and C_6H_6 into 4-*benzoyl*-1-*phenyl*-1 : 2 : 3-*triazole*, m.p. 125° (2 : 4-*dinitrophenylhydrazone*, m.p. 254—255°). Et_2 1-phenyl-1 : 2 : 3-triazole-4 : 5-dicarboxylate, powdered Na, and EtOAc at 100° afford *Et* β-*keto*-β-4-1-*phenyl*-1 : 2 : 3-*triazolylpropionate*, m.p. 115° (2 : 4-*dinotrophenylhydrazone*, m.p. 235—236°), which gives a dark red colour with $FeCl_3$ in EtOH and is hydrolysed by N-KOH–EtOH to (II); it is converted by H_2O at 124—130° or by boiling NaOH–EtOH into 4-*acetyl*-1-*phenyl*-1 : 2 : 3-*triazole*, m.p. 113° (2 : 4-*dinitrophenylhydrazone*, m.p. 251—252°). Me_2 1-phenyl-1 : 2 : 3-triazole-4 : 5-dicarboxylate, COPhMe, and powdered Na in boiling C_6H_6 give 4-*benzoylacetyl*-1-*phenyl*-1 : 2 : 3-*triazole*, m.p. 169—170°, which gives a dark red colour with $FeCl_3$ and a blue-green ppt. with $Cu(OAc)_2$. (I) is converted by $SOCl_2$ into the cryst. chloride (corresponding *anilide*, m.p. 150°) and thence by $AlCl_3$ in C_6H_6 into 4-*benzoyl*-1-*phenyl*-5-*methyl*-1 : 2 : 3-*triazole* (2 : 4-*dinitrophenylhydrazone*, m.p. 246°). Et 1-phenyl-5-methyl-1 : 2 : 3-triazole-4-carboxylate, m.p. 60°, EtOAc, and Na powder at 100° alone and subsequently in presence of C_6H_6 afford 4-*acetyl*-1-*phenyl*-5-*methyl*-1 : 2 : 3-*triazole*, m.p. 99—100° (2 : 4-*dinitrophenylhydrazone*, m.p. 211°). (I) is transformed by HCl–EtOH at room temp. followed by vac.-distillation into *Et* 1-*phenyl*-1 : 2 : 3-*triazole*-4-*carboxylate*, b.p. 210°/22 mm., m.p. 88°. 4-Hydroxy-1-phenyl-1 : 2 : 3-triazo-5 : 6-benzoindene (A., 1939, II, 229) couples with diazotised *p*-toluidine in N-KOH–MeOH to give 4-*hydroxy*-7-p-*tolueneazo*-1-*phenyl*-1 : 2 : 3-*triaza*-5 : 6-*benzoindene*, m.p. 210° (decomp.), converted by glycerol and 82% H_2SO_4 at 150° into 9-*keto*-7 : 8-*azimido*-1′-*phenylperinaphthindene*



(III), m.p. 255—256°. H. W.

αβγδ-Tetraphenylchlorin. M. Calvin, R. H. Ball, and S. Aronov (*J. Amer. Chem. Soc.*, 1943, **65**, 2259).—The "tetraphenylporphin" of Rothemund (A., 1940, II, 27) contains a porphyrin *A* and a chlorin *B* (cf. Aronov *et al.*, A., 1943, II, 343). $Zn(OAc)_2$ in boiling *n*-$C_6H_{13}{\cdot}OH$ (I) converts *A* into its Zn salt (absorption max. at 555, 596, and 618 mμ.), reduced by Na to the phosphorescent Zn salt (absorption max. at 620, 600, and 559 mμ.) of *B*, which gives a green hydrochloride. $Cu(OAc)_2$ in (I) converts *B* into its Cu salt (absorption max. at 536 and 615 mμ.), whence O_2 yields the Cu salt (absorption max. at 538 mμ.) of *A*. R. S. C.

Reaction of *o*-quinoneimmes with alkylidenebisamines and hydrobenzamide. G. McCoy and A. R. Day (*J. Amer. Chem. Soc.*, 1943, **65**, 2157—2159).—Retenequinoneimine with benzylidenebispiperidine (I) in boiling EtOH gives 2-phenylreteneoxazole (II) (100%), with methylenebismorpholine (III) gives 2-morpholinoreteneoxazole (86%), and with hydrobenzamide (IV) (0·33 mol.) gives (II) (92·5%). HCl and (IV) in Et_2O give $CHPh(NH_2)_2{,}HCl$ (2 equivs.). Phenanthraquinoneimine with (I) or (IV) gives 2-phenylphenanthroxazole (98 and 86%, respectively) and with (III) gives 2-morpholinophenanthroxazole (51%). Reaction mechanisms are proposed. R. S. C.

***o*-Condensations which lead to oxazole or iminazole formation.** G. McCoy and A. R. Day (*J. Amer. Chem. Soc.*, 1943, **65**, 2159—2162).—Oxazoles are formed from compounds containing $\cdot CX{:}C{\cdot}N{:}CYR$ (*A*) when X = OH and Y = H, OH, NH_2, NHR, NR_2, or N:CHAr. Glyoxalines are formed when X = NH_2 and Y = H, OH, NH_2, NHR, or NR_2, or X = NHR and Y = H. (*A*) is the common intermediate in many reactions. R. S. C.

2-Phenylthiazole-4 : 5-dicarboxylic acid derivatives. E. Huntress and K. Pfister, tert. (*J. Amer. Chem. Soc.*, 1943, **65**, 2167—3169).—$SH{\cdot}CPh{:}NH$ and $CO_2Et{\cdot}CCl{:}C(OH){\cdot}CO_2Et$ in boiling EtOH give *Et*$_2$ 2-*phenylthiazole*-4 : 5-*dicarboxylate* (83%), m.p. 95·5—96·5°, whence hot KOH–MeOH gives *K H* 2-*phenylthiazole*-4 : 5-*dicarboxylate*, m.p. 258—259·2° (decomp.), and then HCl gives the *dicarboxylic acid* (I), m.p. 190·3—190·8° ($SOCl_2$, not Ac_2O or AcCl, gives the *anhydride*, m.p. 200·3—202·3°). At 165—170° (I) gives 2-phenylthiazole-4-carboxylic acid (91·5%), m.p. 175·7—176·7° (also obtained from the K H salt at 200° and then 265° and from 2-phenyl-4-hydroxymethylthiazole by oxidation). With $N_2H_4{,}H_2O$ in 95% EtOH at 100° (I) gives the *dihydrazide*, sinters ~200°, m.p. 349·5—351·5° [(*CMe*:)$_2$ derivative, m.p. 252·9—253·2°], but on longer heating yields the cyclo*hydrazide*, m.p. 348·5—350·5° (decomp.), which is not chemiluminescent with $K_3Fe(CN)_6$–alkali–H_2O_2. $SH{\cdot}CPh{:}NH$ and $CHO{\cdot}CHCl{\cdot}CO_2Et$ (or the Na salt) in boiling EtOH give *Et* 2-*phenylthiazole*-5-*carboxylate* (37%), m.p. 64·8—65·8°, and thence the *acid*, m.p. 192—193° (gas) (*chloride*, m.p. 125·3—126·5°; *amide*, m.p. 213·7—214·5°). M.p. are corr. (block). R. S. C.

Oxidation of 2-aminobenzthiazoles. W. Kirk, jun., J. R. Johnson, and A. T. Blomquist (*J. Org. Chem.*, 1943, **8**, 557—563).—The appropriate 2-aminobenzthiazole is oxidised by NaOCl in H_2O–dioxan at room temp. to 2-*azobenzthiazole* (I), m.p. 295° (decomp.), and its 6 : 6′-*dimethyl*, m.p. 319° (decomp.), 6 : 6′-*dichloro*-, m.p. 348° (decomp.), 6 : 6′-*dibromo*-, m.p. 338° (decomp.), 6 : 6′-*diethoxy*-, m.p. 290° (decomp.), and 4 : 4-*dimethyl*, m.p. 301° (decomp.), derivatives. These compounds are also obtained by the action of Na_2SnO_2 on 2-*nitro*- (II), m.p. 157—158°, 2-*nitro*-6-*methyl*-, m.p. 131—132°, 2-*nitro*-6-*ethoxy*-, m.p. 151—152°, 6-*chloro*-2-*nitro*-, m.p. 160—161°, 6-*bromo*-2-*nitro*-, m.p. 179—180°, and 2-*nitro*-4-*methyl*-, m.p. 152—153°, -*benzthiazole* prepared according to the scheme:

$$C_6H_3R\langle{}^{S}_{N}\rangle C{\cdot}NH_2 \rightarrow C_6H_3R\langle{}^{S}_{N}\rangle C{\cdot}N_2BF_4 \rightarrow (NaNO_2 + Cu)$$

$$C_6H_3R\langle{}^{S}_{N}\rangle C{\cdot}NO_2.$$

The structure of the NO_2-compounds is confirmed by reducing them to NH_2-derivatives identified as their Ac derivatives. Reduction of the NO_2-compounds by glucose affords 6 : 6′-*dimethyl*-, m.p. 314° (decomp.), 6 : 6′-*dichloro*-, m.p. 344° (decomp.), 6 : 6′-*dibromo*-, m.p. 336° (decomp.), 6 : 6′-*diethoxy*-, m.p. 272° (decomp.), and 4 : 4′-*dimethyl*-, m.p. 293° (decomp.), 2-*azoxybenztriazole*; (II) similarly gives (I). M.p. are block. H. W.

Benzthiazoles etc. See B., 1944, II, 122.

Photochemical synthesis of vitachromes for vital staining.—See A., 1944, III, 237.

2 : 4-Diamino-5-(4′-methyl-5′-β-hydroxyethylthiazolium chloride)-methylpyrimidine hydrochloride, a new analogue of aneurin. W. Huber (*J. Amer. Chem. Soc.*, 1943, **65**, 2222—2226).—$OEt{\cdot}CH{:}C(CN)_2$ [modified prep. from $CH_2(CN)_2$, $CH(OEt)_3$, and Ac_2O at 110—95°; 72·6% yield], m.p. 67—68°, and guanidine (prep. from the nitrate *in situ*) in EtOH at <15° (cooling) give 2 : 4-*diamino*-5-*cyanopyrimidine* (54%), m.p. 318° (decomp.) [*monohydrochloride*, m.p. >360°; picrate, m.p. 281—283° (decomp.)], which with boiling Ac_2O gives the *Ac*$_1$, m.p. 238°, and with Ac_2O at 200° gives the *Ac*. derivative, m.p. 197—198°, and with H_2–NH_3–MeOH–Raney Ni at room temp./60 lb. (or 200 lb.; less well, PtO_2 or Pd–ZrO_2) gives 2 : 4-diamino-5-aminomethylpyrimidine (81%) [*dihydrochloride* (I),

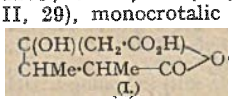
m.p. 278—280° (decomp.)], and some di-(2 : 4-diamino-5-pyrimidylmethyl)amine [*tetrahydrochloride* (II), m.p. 357° (decomp.); obtained as sole product by Pd–ZrO_2 in aq. HCl]. Neutralisation of (II) in H_2O by 10% NaOH gives NH_3 and 2 : 4-diamino-5-hydroxymethylpyrimidine (90%), m.p. 265° (decomp.) [*hydrochloride*, m.p. 327° (decomp.); picrate, m.p. 244—246° (decomp.)]. Treating (I) in H_2O with aq. K_2CO_3 and then aq. HCS_2K at <15° gives 2 : 4-*diamino-5-thioformamidomethylpyrimidine* (III) (86%), m.p. 181—182° (decomp.) [*monohydrochloride*, m.p. 205—206° (decomp.)]. $CHAcBr{\cdot}[CH_2]_2{\cdot}OH$ (modified prep.; irritant) and (III) in HCO_2H at 40°, rising to 60°, give, after hydrolysis by 5% HCl at 40°, 3-2′ : 4′-*diamino-5′-pyrimidylmethyl-4-methyl-5-β-hydroxyethylthiazolium chloride hydrochloride* (IV), m.p. 245—247° [corresponding *bromide hydrobromide*, m.p. 214—216° (decomp.)]. 25-γ doses of (IV) have no vitamin-B_1 activity. Colorimetric analysis of (IV) is inaccurate (cf. C., 1944, Part 2). R. S. C.

VII.—ALKALOIDS.

Gelsemine. I. Degradation of gelsemine to 2 : 3-dimethylindole. L. Marion (*Canad. J. Res.*, 1943, **21, B**, 247—250).—Gelsemine, m.p. 179°, is degraded by soda–lime or black Se at 320° to a mixture of bases and neutral products in the latter of which the presence of 2 : 3-dimethylindole (picrate, m.p. 153°) has been established. The bases afford picrates, m.p. 210° (softens somewhat at 202°) and m.p. 238° (decomp.) after softening, in quantity too small for investigation. H. W.

Alkaloids of *Lycopodium* species. IV. *L. tristachyum*, Pursh. L. Marion and R. H. F. Manske (*Canad. J. Res.*, 1944, **22, B**, 7—4).—The following alkaloids have been extracted from *L. tristachyum*, Pursh: nicotine; lycopodine, m.p. 116° (perchlorate, m.p. 279°); alkaloid *L*13 (*perchlorate*, $C_{16}H_{25}ON,HClO_4$, m.p. 274°), also found in *L. obscurum*; alkaloid *L*14 (*perchlorate*, $C_{14}H_{28}N,HClO_4$, m.p. 238°); alkaloid *L*15 (*perchlorate*, $C_{20}H_{31}O_4N,HClO_4$, m.p. 231°). M.p. are corr. H. W.

Structure of monocrotaline. X. Monocrotalic acid. R. Adams and J. M. Wilkinson, jun. (*J. Amer. Chem. Soc.*, 1943, **65**, 2203—2208; cf. A., 1944, II, 87).—Contrary to previous views (A., 1940, II, 29), monocrotalic acid is probably (I). The Legal test, not



given by Me anhydromonocrotalate (II), is not sp. for βγ-unsaturated γ-lactones. With boiling HCl–MeOH, (I) gives Me monocrotalate (III) (40%) and some (II). Further, (III) and its analogues in aq. NH_3 rapidly give the amides. Boiling $SOCl_2$ converts (I) into the *chloride* (IV), m.p. 145—146°, whence hot MeOH gives (III), but longer heating gives, after hydrolysis in air, *anhydromonocrotalic acid*, m.p. 115—117° (or sometimes an oil), $[\alpha]_D$ +196·0° in EtOH, hydrogenated (Raney Ni; Et_2O; 125°/2000 lb.) to the known H_2-acid (V). With CH_2N_2–Et_2O, (IV) gives the *diazo-ketone*, m.p. 132—134° (decomp.), which with Ag_2O etc. gives tars but with 1 : 1 conc. HCl–H_2O gives a *Cl-ketone*, m.p. 97—99°, the Cl of which resists H_2–Pd. Boiling HNO_3 (*d* 1·42) oxidises (I) to $(CMe{\cdot}CO)_2O$ and a little Ac_2, but only AcOH is obtained by $KMnO_4$. In 16N. aq. NH_3, (III) gives *monocrotalamide* (VI), m.p. 209—211°; *anhydro-*, m.p. 146—147°, and *dihydroanhydro-monocrotalamide*, softens 125°, m.p. 130—132°, are similarly prepared. Interaction of KCN with Me dihydroanhydromonocrotalate in H_2SO_4–MeOH (cf. Ranganathan, A., 1937, II, 398) gives, after hydrolysis, only a *form*, m.p. 111—112°, $[\alpha]_D^{27}$ −55·7° in EtOH, of (V). *Et H* cis-*αβ-dimethylsuccinate* (prep. from the anhydride by hot EtOH), b.p. 115—117°/3 mm., and PCl_5 at room temp. and then 100° give the acid *chloride*, b.p. 96—97°/15 mm., addition of which in Et_2O to $CN{\cdot}CHNa{\cdot}CO_2Et$–$Et_2O$ gives *Et*$_2$ *β-keto-α-cyano-γδ-dimethyladipate* (42%), b.p. 136—138°/2 mm., which did not yield (VI). $CHAc{:}CH{\cdot}CO_2Et$, b.p. 65—67°/2 mm. (*semicarbazone*, m.p. 205—207°), $CHMeBr{\cdot}CO_2Et$, and Zn in boiling C_6H_6–PhMe give (?) *Et β-hydroxy-δ-carbethoxy-αβ-dimethyl-*Δ^{γ}*-pentenoate* (30%), b.p. 121—122°/2 mm., stable to $POCl_3$ or P_2O_5–C_6H_6. M.p. are corr. R. S. C.

VIII.—ORGANO-METALLIC COMPOUNDS.

Organo-boron–nitrogen compounds. III. Reactions of *p*-anisidine, benzylamine, and nitrobenzene with boron chloride. C. R. Kinney and C. L. Mahoney (*J. Org. Chem.*, 1943, **8**, 526—531).—Gradual addition of BCl_3 to *p*-$OMe{\cdot}C_6H_4{\cdot}NH_2,HCl$ (I) suspended in C_6H_6 at 0° and then at room temp. gives the *salt* (II), *p*-$OMe{\cdot}C_6H_4{\cdot}NH_2,BCl_3$, m.p. 108°, softens at 105° when slowly heated, m.p. 110° (decomp.), softens at 105° when rapidly heated. In boiling C_6H_6 it loses 2 HCl with formation of *trichlorotri-p-anisyltriboron nitride*, $RN\langle^{BCl{\cdot}NR}_{BCl\,NR}\rangle BCl$ (R = *p*-$C_6H_4{\cdot}OMe$) (also +1C_6H_6), m.p. 229—235° (vac.; decomp.). This is hydrolysed by cold H_2O apparently to the corresponding OH-compound and by boiling H_2O completely to *p*-$OMe{\cdot}C_6H_4{\cdot}NH_2$ and H_3BO_3. When heated with an excess of the base BCl_3 yields *B tri-*p*-anisidide*, m.p. 124°, relatively stable in air but rapidly hydrolysed by boiling H_2O; with HCl in C_6H_6 it appears to give a mixture of (I) and (II). $CH_2Ph{\cdot}NH_2$ and BCl_3 in dry C_6H_6 give a good yield of the additive *product* (III), m.p. 166—167°, decomp. '>185°. On concentrating the C_6H_6 solution only a small quantity of needles which rapidly changed to plates separated in place of the expected trimeride. BCl_3 is converted by excess of $CH_2Ph{\cdot}NH_2$ in boiling C_6H_6 into $CH_2Ph{\cdot}NH_2,HCl$ and a compound, m.p. 145°, containing N but not B or Cl; this last compound does not result in boiling xylene. $PhNO_2,BCl_3$, m.p. 45—47° in a sealed capillary, is obtained directly from its components; it is very sensitive to moist air. H. W.

Organic compounds of mercury. XXI. Properties and structure of mercury derivatives of acetylene. R. H. Freidlina (*Bull. Acad. Sci. U.R.S.S.*, 1942, *Cl. Sci. chim.*, 14—20).—The *compounds*, $CHCl{:}CH{\cdot}HgX$ (I), where X = Br, m.p. 121—122°; CN, m.p. 101—102°; OBz, m.p. 120—122°; $\cdot C{:}CPh$, m.p. 102—103°; $\cdot N(CO)_2C_6H_4$-*o*, m.p. 166—167° (all with decomp. at m.p.), and OAc, no m.p., decomp. ~85°, are pptd. from the strongly alkaline solution [presumably containing (I) (X = OH)] obtained from an aq. suspension of (I) (X = Cl) and Ag_2O. The *complex*, $CHCl{:}CH{\cdot}HgCl,C_5H_5N$, m.p. 84° (decomp.), is formed from (I) (X = Cl) in EtOH. C_2H_2 is liberated from (I) by the action of HCl, KI, KCN, and *o*-allylphenol, also from (I) (X = Cl, CN) on heating above the m.p. R. C. P.

IX.—PROTEINS.

Rate of liberation of cystine from proteins by acid hydrolysis. W. C. Hess and M. X. Sullivan (*Arch. Biochem.*, 1943, **3**, 53—60).—Wool, finger nail, lactalbumin, gliadin, edestin, and α-globulin (lima bean) were hydrolysed with 20% HCl, 1 : 1 HCl–HCO_2H, and HI, and the liberated cystine was determined at intervals. The max. vals. for each protein were the same by the three reagents. No humin was formed with HI, but hydrolysis was slower with the HCl–HCO_2H than with HI or HCl. The hydrolysis of wool by HCl is a second-order reaction up to 90% liberation of cystine. The S in wool is probably combined in at least two forms, RS·SR and RSR′. E. R. S.

Cysteine, cystine, and methionine content of proteins. W. C. Hess and M. X. Sullivan (*J. Biol. Chem.*, 1943, **151**, 635—642).—Practically all the S of 7 out of 10 unhydrolysed proteins is accounted for by cysteine (I), cystine, and methionine, whilst 85, 82, and 87% are accounted for in calf globin, edestin, and squash-seed globulin, respectively. Of the S of squash-seed globulin ~13% is lost during hydrolysis in an unknown form. Total ·SH in unhydrolysed protein agrees with the (I) determined in the acid hydrolysate, indicating that (I) complexes are present in the native protein. H. G. R.

Amino-acid yield from various animal and plant proteins after hydrolysis of fat-free tissue.—See A., 1944, III, 349.

Dispersion of keratins. II. Dispersion of keratins by reduction in neutral solutions of protein denaturants. C. B. Jones and D. K. Mecham (*Arch. Biochem.*, 1943, **3**, 193—202; cf. A., 1944, II, 88).—Vals. are given for moisture, ash, N, S, cystine, and cysteine in the keratins from chicken and duck feathers, tortoise scutes, snake skin, cattle hoof and horn, wool, pig and human hair, and ovokeratin. The keratins are dispersed in neutral solution at 40° for 18 hr. by cleavage of their –S·S– linkings by thioglycol, $SH{\cdot}CH_2{\cdot}CO_2H$, or $NaHSO_3$, in presence of $CO(NH_2)_2$, guanidine, NH_4CNS, $HCO{\cdot}NH_2$, NH_2Ac, $CS(NH_2)_2$, or detergents of the Na alkyl sulphate type. The neutral keratin dispersions are clear liquids of low η. The dispersed protein is pptd. by $MgSO_4$ or $(NH_4)_2SO_4$, acidification, addition of protein precipitants, or by dialysis. In some cases increase of the pH val. to 8 causes pptn., whilst in others addition of H_2O has the same effect. The extent of dispersion depends on the size of the keratin particles. The various keratins differ in their degree of dispersal in neutral solution, and also with particular combinations of reducing and dispersing agents. Feather keratin is most readily dispersed in neutral solution, whilst ovokeratin is exceptionally resistant to dispersion not only in neutral solution, but also in alkaline reducing solutions. J. N. A.

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A II—Organic Chemistry.

JUNE, 1944.

I.—ALIPHATIC.

Fluorinated derivatives of propane. V. A. L. Henne and J. V. Flanagan (*J. Amer. Chem. Soc.*, 1943, **65**, 2362—2363; cf. A., 1942, II, 126).—HgO–HF (apparatus: C., 1944, Part 3) replaces Cl by F in C_3H_8 derivatives, including those containing H. In CCl_2RR' gradual change of R = Me to R = CCl_3 progressively hinders and finally prevents the changes, $CCl_2 \rightarrow CClF \rightarrow CF_2$. A central CF_2 usually has little effect on the ease of fluorination of an adjacent CCl_3. 1 mol. of HgO suffices to introduce 2 F. 10—12 mols. of HF are used, the excess acting as solvent. The reactants, precooled to −78°, are mixed at −78° and left to warm up or heated for reaction. Recovery of Hg, best as HgO, is described. Yields may be up to 86%. $CH_2Cl{\cdot}CMeCl_2$ at room temp. gives 51% of $CH_2Cl{\cdot}CMeF_2$. $CCl_2(CH_2Cl)_2$ at 125° (6 hr.) gives *αβγ-trichloro-β-fluoro-*, m.p. −67·8°, b.p. 130·80°, and then *αγ-dichloro-ββ-difluoropropane* (**I**), m.p. −30·04°, b.p. 96·69°, structures being proved by chlorination of (**I**) in light to *aaγ-trichloro-ββ-difluoropropane*, m.p. −60·80°, b.p. 127·27°, and then $CCl_3{\cdot}CF_2{\cdot}CH_2Cl$, m.p. −17·13°, b.p. 151·18°, and $CF_2(CCl_3)_2$. $CH_2Cl{\cdot}CCl_2{\cdot}CHCl_2$ gives with decomp. a little monofluoride (not purified) and (?) $CHClF{\cdot}CClF{\cdot}CH_2Cl$, a glass. $CCl_3{\cdot}CMeCl_2$ (**II**) [a commercial product, erroneously stated to be $CHCl(CHCl_2)_2$] at 100° gives a solid solution of $CCl_3{\cdot}CMeClF$, m.p. 102·4°, b.p. 138·2—138·6°, with a little $CCl_2F{\cdot}CMeCl_2$; further fluorination of (**II**) gives *aaββ-trichloro-αβ-difluoropropane*, m.p. 27·6°, b.p. 97·7°, which is also obtained from $CCl_3{\cdot}CMeClF$ and with Cl_2 in light gives *aaβγγγ-hexachloro-αβ-difluoropropane*, m.p. −55°, b.p. 196·0°. $CCl_3{\cdot}CMeF_2$ yields very readily 86% of *α-chloro-aaββ-tetrafluoropropane*, m.p. −74·72°, b.p. 19·93°, which is very slowly chlorinated to $CCl_3{\cdot}CF_2{\cdot}CClF_2$ (**III**), m.p. −92·78°, b.p. 113·95°. $CCl_3{\cdot}CF_2{\cdot}CH_2Cl$ yields at 135° (6—8 hr.) 50% of $CClF_2{\cdot}CF_2{\cdot}CH_2Cl$, m.p. −75·0°, b.p. 68·2°, readily converted into (**III**). $CCl_2F{\cdot}CF_2{\cdot}CH_2Cl$, m.p. −79·8°, b.p. 109·5°, and $CCl_3{\cdot}CHCl{\cdot}CH_2Cl$, b.p. 192·5—193°, are also reported. R. S. C.

Use of semi-micro-technique in elementary organic chemistry. II. N. D. Cheronis, P. G. Arvan, and H. Teifeld (*J. Chem. Educ.*, 1943, 20, 431—437; cf. A., 1939, II, 192).—Apparatus for ordinary, fractional, and steam distillations is described. The semi-micro-prep. of decane, *cyclo*hexene, and Bu$^{\alpha}$Br is given. L. S. T.

Ozonisation of terminal groups of saturated hydrocarbons of the aliphatic series.—See A., 1944, I, 131.

Photochemical chlorination and photochemical oxidation of tetrachloroethylene sensitised by chlorine.—See A., 1944, I, 132.

Unique polyene pigment of the marine diatom *Navicula torquatum*.—See A., 1944, III, 370.

Conjugated systems. XX. Reaction of chloroprene with iodine chloride. XXI. Reaction of αβ-dichlorobutadiene with hypobromous acid and alkyl hypoiodites. Synthesis and properties of αchlorovinylethylene oxide and αβ-dichloro-γ-alkoxybutadienes. XXII. Order of addition of bromine to bromoprene. Synthesis and properties of αβ-dibromo-Δ$^{\alpha\gamma}$-butadiene. A. A. Petrov (*J. Gen. Chem. Russ.*, 1943, **13**, 155—158, 230—236, 237—241).—XX. Chloroprene and ICl in $CHCl_3$ at −5° yield chiefly $CHCl{:}CH{\cdot}CHCl{\cdot}CH_2I$.

XXI. $CH_2{:}CH{\cdot}CCl{:}CHCl$ (**I**) and aq. NHBrAc in 1% H_2SO_4 yield *αβ-dichloro-δ-bromo-Δ$^{\alpha}$-buten-γ-ol*, b.p. 100—106°/10 mm. (*acetate*, b.p. 109—112°/10 mm.), from which *αβ-dichloro-γδ-oxido-Δ$^{\alpha}$-butene*, b.p. 94—95·5°/85 mm., is obtained by distillation at 150° from 80% aOH. This with 50% H_2SO_4 at 60° yields *αβ-dichloro-Δ$^{\alpha}$-buteneαδ-diol*, b.p. 135—136°/10 mm. (*diacetate*, b.p. 128·5—129°/10 mm.). (I) and I in MeOH or EtOH in presence of HgO afford *αβ-dichloro-δ-iodo-γ-methoxy-*, b.p. 90—91·5°/5 mm., or *-γ-ethoxy-Δ$^{\alpha}$-butene*, b.p. 94·5—95°/5 mm. (decomp.). These ethers are converted by heating with 20% KOH in EtOH into *αβ-dichloro-γ-methoxy-*, b.p. 90·5—91·5°/85 mm., or *-γ-ethoxy-Δ$^{\alpha\gamma}$-butadiene*, b.p. 103·5—105°/85 mm., from which *Me αβ-dichlorovinyl ketone*, b.p. 61·5—62°/30 mm., is obtained by hydrolysis with 5% H_2SO_4 at 40°.

XXII. Bromoprene and Br in $CHCl_3$ at 10—15° yield *αβδ-tribromo-Δβ-butene*, b.p. 121—122°/10 mm. This with KOH in EtOH at 0° gives *αβ-dibromo-Δ$^{\alpha\gamma}$-butadiene*, b.p. 46—46·5°/10 mm.; when the reaction is conducted in boiling solution $(CH{:}C)_n$ is also produced. R. T.

Raman spectra of two forms of *allo*ocimene.—See A., 1944, I, 118.

Sesquiterpenes. LXI. Synthesis of an aliphatic sesquiterpene alcohol with irregular isoprene chain. H. Schinz and P. H. Muller (*Helv. Chim. Acta*, 1944, **27**, 57—60; cf. A., 1943, II, 181, 182).—Geranylacetone, b.p. 126—130°/11 mm., condenses with 33% CH_2O and $Ba(OH)_2{,}2H_2O$ in EtOH at 60° to *α-hydroxymethylgeranylacetone* (**I**), b.p. 122°/0·15 mm. [*allophanate*, m.p. 99—100°, from which (**I**) is not readily regenerated; non-cryst. semicarbazone], converted by MgMeI into *βζκ-trimethyl-ι-hydroxymethyl-Δ$^{\beta\zeta}$-undecadien-κ-ol*, b.p. 134—137°/0·07 mm. This is dehydrated by *o*-$C_6H_4(CO)_2O$ at 180° with a short period at 190° to *βζκ-trimethyl-ι-hydroxymethyl-Δ$^{\beta\zeta\kappa}$-undecatriene*, b.p. 88°/0·02 mm., 154°/12 mm., which absorbs 3 mols. of H_2 and has an odour reembling that of farnesol. H. W.

Interaction of hydroxy-compounds and phosphorus and thionyl halides in the absence and presence of tertiary bases. I. Optically active β-octanol, ethyl mandelate, and phenylmethylcarbinol. W. Gerrard (*J.C.S.*, 1944, 85—90).—Addition of PCl_3 to (+)-β-octanol (**I**) and to (−)-OH·CHPh·CO_2Et (**II**) gives the chloride, RCl, and the H phosphite, $P(OR)_2{\cdot}OH$. Reversed order of mixing gives the chlorophosphite, $PCl_2{\cdot}OR$, which did not decompose to RCl. PCl_3 mixed with (−)-CHPhMe·OH (**III**) in either order gives (+)-CHPhMeCl (**IV**) without chlorophosphite. (−)-*Tri-β-octyl phosphite* and PCl_3 give an equilibrium mixture of the two chlorophosphites $PCl_2{\cdot}OR$ and $PCl(OR)_2$ and PCl_3. $SOCl_2$ mixed in either order with (**I**) and (**II**) gives an equilibrium mixture of the chlorosulphinate OR·SOCl (**V**), the sulphite R_2SO_3 (**VI**), and $SOCl_2$. $SOCl_2$ and (**III**) give only (**IV**). With C_5H_5N in Et_2O (**I**), (**II**), and (**III**) on addition of PCl_3 give the corresponding phosphites; with $SOCl_2$ (same conditions) (**I**) and (**II**) give the corresponding sulphites but (**III**) gives (**IV**) and no sulphite. (**III**) with Et chlorosulphinate gives (−)-*α-phenylethyl Et sulphite*, which with $SOCl_2$ gives the non-inverted CHPhMeCl. $SOCl_2$ and (+)-di-β-octyl sulphite give an equilibrium mixture of (**V**), (**VI**), and $SOCl_2$. Mechanisms depending on oriented collisions on the " front " or on the " back " of the asymmetric C are discussed. Compounds described include: (−)-*β-octyloxyphosphorus dichloride*, b.p. 83—84°/2 mm. 118—119°/17 mm., $[\alpha]_D^{18}$ −34·5°; (+)-*di-β-octyloxyphosphorus chloride*, b.p. 135—140°/2 mm., $[\alpha]_D^{8}$ +0·7°; (+)-*β-octyl H_2 phosphite*, $[\alpha]_D^{16}$ +7·0°; (+)-*di-β-octyl H phosphite*, b.p. 138—140°/2 mm., $[\alpha]_D^{18}$ +15·8°; (−)-*tri-β-octyl phosphite*, b.p. 162—164°/2 mm., $[\alpha]_D^{19}$ −0·8°; (−)-*α-carbethoxybenzyloxyphosphorus dichloride*, b.p. 105—108°/2 mm., α_D −122·9°; (+)-*bis-α-carbethoxybenzyl sulphite*, b.p. 218—221°/2 mm., $[\alpha]_D^{22}$ +124·1; (−)-*α-phenylethyl Et sulphite*, b.p. 93°/2—3 mm., $[\alpha]_T^{20}$ −94·5°. (Vals. of α are for *l* = 10 cm.). D. G.

Stabilisation of polysulphones towards heat. C. S. Marvel and W. H. Sharkey (*J. Org. Chem.*, 1944, **9**, 113—116).—Polysulphones made from olefines containing a trace of $CH_2{:}CH{\cdot}CH_2Br$ (**I**) are much more stable towards heat than polysulphones made from pure olefines. The preformed polysulphone can also be treated with (**I**) to cause some stabilisation but the effect is less marked. The effect appears sp. for (**I**) and is not shown by $CH_2{:}CH{\cdot}CH_2Cl$, EtBr, $CH_2{:}CH{\cdot}CH_2{\cdot}OH$, $CH_2{:}CH{\cdot}[CH_2]_2{\cdot}Br$, camphene, α-bromoheptene, undecylenyl bromide, $CHPh{:}CHBr$, $CH_2{:}CH{\cdot}CO_2Et$, $COEt{\cdot}CH_2Cl$, $CHCl_3$, $C_7H_{15}{\cdot}SH$, CCl_4, *p*-$C_6H_4Br{\cdot}CH_2Cl$, CH_2PhCl, $CH_2Ph{\cdot}OH$, furfuryl alcohol, furfurylacrylic acid, and chloro*iso*durene. Heat-treatment of polysulphones appears to remove some of the readily decomposable material so that the residue is more stable towards heat. Dissolution and repptn. also improves the thermal stability to some extent. Presence of peroxides in polysulphones increases the amount of decomp. which occurs when they are heated. H. W.

Use of phenyl esters in the Reformatsky reaction.—See A., 1944, II, 162.

Union of gaseous oxygen with methyl oleate at 20° and 120°. D. Atherton and T. P. Hilditch (*J.C.S.*, 1944, 105—107).—The products of autoxidation in O_2 of Me oleate are partly separated by adsorption on SiO_2 gel, and then oxidised ($KMnO_4$ in $COMe_2$) and the scission products examined. At 20° the main products are suberic (**I**), octoic (**II**), azelaic (**III**), and nonoic acids (**IV**), confirming peroxidation at the ·CH_2· groups adjacent to the double linking (cf. Farmer, A., 1943, I, 151). At 120°, only (**III**) and (**IV**) and a trace of (**I**) were isolated, with no (**II**), as well as more complex products, suggesting action at the double linking. D. G.

Normal aliphatic β-hydroxy- and α-keto-acids. F. Adickes and G. Andresen (*Annalen*, 1943, **555**, 41—56).—The prep. of β-OH-acids by diazotisation of β-NH_2-acids could not be successfully accomplished and ozonisation of allylalkylcarbinols gives only poor yields. Condensation of the aldehydes with 2 fewer C atoms with $CH_2Br{\cdot}CO_2Et$ (Reformatzky) and hydrolysis of the esters gives the OH-acids in 10—12% yield. The following are described: β-hydroxy-valeric, m.p. 43—44° (*Et* ester, b.p. 83—85°/10 mm.); -hexoic, m.p. 13°; *-heptoic*, m.p. 40—41° (*Et* ester, b.p. 94—96°/5 mm.); *-octoic*, m.p. 38—38·5° (*Et* ester, b.p. 101—104°/5 mm.); -nonoic; -decoic, m.p. 56—56·5°; *-undecoic*, m.p. 73—73·5°, softens at 72°; *-lauric acid*, m.p. 70—70·5°, softens at 69°. α-CO-acids up to C_{10} are obtained by prolonged condensation at room temp. (shortened by boiling under a reflux condenser) of the requisite ester with $Et_2C_2O_4$ and NaOEt in Et_2O. For esters of higher mol. wt. KOEt in C_5H_5N is used as condensing agent. The esters are hydrolysed and decarboxylated by boiling HCl. Thus are obtained: α-keto-valeric, m.p. 6—7°, softens at 5° (*Ba* salt; *Et α-ketovalerate* 2 : 4-*dinitrophenylhydrazone*, m.p. 116—116·5°, softens at 115°); *-hexoic*, b.p. 101—102°/20 mm., m.p. 7—8° [*Ba* salt; oxime, m.p. 132—133° (decomp.), softens at 129°; *phenylhydrazone*, m.p. 84—86°, softens at 80°; *Et α-ketohexoate* 2 : 4-*dinitrophenylhydrazone*, m.p. 117—118°, softens at 114°]; *-iso*hexoic, b.p. 92—94°/20 mm.; *-heptoic*, m.p. 29—30° (*Ba* salt; *oxime*, m.p. 126—127°, softens at 125°; *phenylhydrazone*, m.p. 102—103°; *Et* ester, b.p. 87—88°/8 mm., and its 2 : 4-*dinitrophenylhydrazone*, m.p. 102—103°); -octoic, m.p. 32—33°, b.p. 118—123°/13 mm., 104°/6 mm.; -nonoic, m.p. 43—44°, softens at 42° (*Na* salt; oxime, m.p. 98—98·5°, softens at 97°; *Et α-ketononoate* 2 : 4-*dinitrophenylhydrazone*, m.p. 86—87°, softens at 85°); -decoic, m.p. 46—47°, b.p. 148—151°/18 mm. (oxime, m.p. 85—86°, softens at 80°; 2 : 4-dinitrophenylhydrazone, m.p. 134°, softens at 132°); *-undecoic*, m.p. 55°, softens at 52° (*oxime*, m.p. 85—86°, softens at 83°; *Et α-ketoundecoate* 2 : 4-*dinitrophenylhydrazone*, m.p. 86°, softens at 85°); *-lauric*, m.p. 56·5—57°, softens at 56° (*oxime*, m.p. 80—81°, softens at 77°; *Et α-ketolaurate* 2 : 4-*dinitrophenylhydrazone*, m.p. 86°, softens at 83°); *-tridecoic*, m.p. 62—62·5° (*oxime*, m.p. 86—86·5°, softens at 84°; *phenylhydrazone*, m.p. 91—92°, softens at 88°; *Et α-ketotridecoate* 2 : 4-*dinitrophenylhydrazone*, m.p. 84—84·5°, softens at 83°); *-pentadecoic acid*, m.p. 68—68·5°, softens at 66° (*oxime*, m.p. 88—88·5°, softens at 87°; *Et α-ketopentadecoate* 2 : 4-*dinitrophenylhydrazone*, m.p. 86—87°, softens at 84°). The following are incidental: *Et*, α-*oxalbutyrate*, b.p. 84—85°/0·7 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 98—99°, softens at 96°); *Et*$_2$ α-*oxalvalerate* 2 : 4-*dinitrophenylhydrazone*, m.p. 85—86°; *Et*$_2$ α-*oxalhexoate*, b.p. 118—122°/mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 84—85°); *Et*, α-*oxalheptoate*, b.p. 135—140°/1 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 82—83°); *Et*$_2$ α-*oxaloctoate* 2 : 4-*dinitrophenylhydrazone*, m.p. 62—63°, softens at 61°; *Et*, α-*oxalnonoate* 2 : 4-*diphenylhydrazone*, m.p. 65—66°, softens at 64°; *Et*$_2$ α-*oxalmyristate* 2 : 4-*dinitrophenylhydrazone*, m.p. 74—75°. H. W.

Monocrotalic acid.—See A., 1944, II, 147.

α-Alkylthiol-aliphatic acids. A. J. Hill and E. W. Fager (*J. Amer. Chem. Soc.*, 1943, **65**, 2300—2301).—Adding a trace of cryst. KI and then, dropwise, $CHRBr{\cdot}CO_2H$ (I) in 50% EtOH to KOH (1) and R'SH (1 mol.) in boiling EtOH–N_2 gives 70—80% (crude) of α-n-*dodecylthiol-n-undecoic*, m.p. 46—48°, α-n-*tetradecylthiol*-n-*butyric*, m.p. 38—39°, and α-n-*hexadecylthiol-acetic*, m.p. 73·5—74°, *-propionic*, m.p. 58—59°, -n-*valeric*, m.p. 47·5—49°, -n-*hexoic*, m.p. 48·5—49·5°, -n-*decoic*, m.p. 42—43°, -n-*undecoic*, m.p. 47—49°, -n-*dodecoic*, m.p. 46—48°, -n-*tetradecoic*, m.p. 46—48°, and *-palmitic acid*, m.p. 46—48°. When R = H—Bu, the products crystallise from light petroleum, but the higher SH-acids gelatinise and are purified by way of the *Ba* salts. R. S. C.

Derivatives of ω-hydroxybutanal. R. Paul (*Compt. rend.*, 1942, **215**, 303—305).—Pentane-αβε-triol (I) is converted into αβ-iso*propylidenedioxypentan*-ε-*ol*, b.p. 117—118°/12 mm., transformed by $NaNH_2$ into the Na derivative, which with CH_2PhCl in boiling PhMe affords ε-*benzyloxy*-αβ-iso*propylidenedioxypentane*, b.p. 170—171°/11 mm. This is hydrolysed by 0·25N-H_2SO_4 at 40° to ε-*benzyloxypentane*-αβ-*diol*, b.p. 188—190 /5 mm., which is readily oxidised by $Pb(OAc)_4$ at room temp. to *γ-benzyloxybutanal*, b.p. 143°/10 mm. (p-*nitro*-, m.p. 88°, and 2 : 4-*dinitro-phenylhydrazone*, m.p. 94—95°). It is oxidised by Ag_2O to *Ag γ-benzyloxybutyrate*, m.p. 200°. *γ-Chlorobutanal*, b.p. 50—51°/13 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 134—135°), is obtained by oxidising [$Pb(OAc)_4$ or $NaIO_4$] the mixture of ε-chloropentane-αβ-diol and β-chloropentane-αε-diol prepared by the action of AcCl on αδ-epoxypentan-ε-ol. It appears to be polymerised readily by heat. Its *oxime*, m.p. 74·5°, is isomerised by Raney Ni at ~100° to *γ-chlorobutyramide*, m.p. 99—100°. (I) in anhyd. Et_2O is readily oxidised by $Pb(OAc)_4$ to $OH{\cdot}[CH_2]_3{\cdot}CHO$, b.p. 65—68°/10 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 104°; *oxime*, b.p. 147°/12 mm.). It is reduced by Na–Hg to $OH{\cdot}[CH_2]_4{\cdot}OH$ and oxidised by excess of Ag_2O at room temp. to *Ag γ-hydroxybutyrate*, m.p. 178—180°. It is converted by 1% HCl–MeOH into 2-*methoxytetrahydrofuran*, b.p. 105—107°/760 mm., in very poor yield. H. W.

Solubilities of normal aliphatic primary amines of high mol. wt.—See A., 1944, I, 123.

Amino-alcohols. XIII. Synthesis of aliphatic amino-alcohols of pharmacological interest. I. W. C. Gakenheimer and W. H. Hartung (*J. Org. Chem.*, 1944, **9**, 85—88).—Electrolytic reduction of NO_2-alkanols (I) gives good yields of the corresponding NH_2-alkanols (II). Raney Ni in presence of CO_2 or AcOH catalyses the hydrogenation of (I) to (II). If reduction is effected in a neutral solvent (I) undergoes fission of the alkane chain with the formation of primary and *sec.* amines. Evidence indicates that fission takes place with some partly hydrogenated product. The following are reported: γ-nitroheptan-δ-ol, b.p. 122—123°/18 mm.; β-nitro-β-methylhexan-γ-ol, b.p. 122—123°/21 mm.; ε-nitro-octan-δ-ol, b.p. 123—124°/13 mm.; *α-nitro-γ-ethylpentan-β-ol*, b.p. 109—111°/26 mm.; *β-nitro-δ-ethylhexan-γ-ol*, b.p. 118—120°/22 mm.; *α-nitroheptan-β-ol*, b.p. 118—120°/24 mm.; *β-nitro-octan-γ-ol*, b.p. 133—134°/22 mm.; *γ-nitrononan-δ-ol*, b.p. 142—143°/23 mm.; *α-nitro-octan-β-ol*, b.p. 130—132°/24 mm.; β-nitrononan-γ-ol, b.p. 134—136°/23 mm.; *β-amino-δ-ethylhexan-γ-ol*, b.p. 110—112°/27 mm. (*Bz* derivative, m.p. 151°); *γ-aminoheptan-δ-ol*, b.p. 98—99°/20 mm. (*Bz* derivative, m.p. 145°); *α-amino-octan-β-ol*, b.p. 130—132°/26 mm. (*Bz* derivative, m.p. 158°); ε-*amino-octan-δ-ol*, b.p. 118—119°/26 mm. (*Bz* derivative, m.p. 149—150°); *γ-aminononan-δ-ol*, b.p. 116—118°/27 mm. (*Bz* derivative, m.p. 161°). H. W.

Amino-acids. II. Alanine. J. H. Billman and E. E. Parker (*J. Amer. Chem. Soc.*, 1943, **65**, 2455—2456; cf. A., 1943, II, 253).—$NH_2{\cdot}CHMe{\cdot}CH_2{\cdot}OH$ affords a phthalimide derivative only with difficulty, but, when treated with BzCl in presence of Na_2CO_3 in C_6H_6 at ≯10° and then kept at 0°, gives *β-benzamido*-n-*propyl alcohol* (90—91%), m.p. 107—108°, which (crude) with $KMnO_4$ in aq. NaOH at ≯40° gives $NHBz{\cdot}CHMe{\cdot}CO_2H$ (65—70%), m.p. 166°, and thence (boiling 18% HCl) alanine (70—71%). R. S. C.

Solubilities of normal aliphatic nitriles of high mol. wt.—See A., 1944, I, 122.

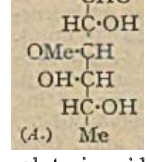
Preparation of malononitrile. A. R. Surrey (*J. Amer. Chem. Soc.*, 1943, **65**, 2471—2472).—70—72% yields are obtained by boiling $CN{\cdot}CH_2{\cdot}CO{\cdot}NH_2$ (1260 g.), $POCl_3$, (800 ml.), and NaCl (1 kg.) in $(CH_2Cl)_2$ (5 l.) for 8 hr. R. S. C.

II.—SUGARS AND GLUCOSIDES.

Theory of a method for comparing the structures of certain compound sugars. Probable relationship of turanose to maltose. C. S. Hudson (*J. Org. Chem.*, 1944, **9**, 117—120).—The keypoint of the method is the symmetry about the central point of mannitol, threitol, the active tartaric acids, and iditol. From this viewpoint are discussed the correlation of natural gentiobiose with synthetic 1-β-*D*-glucopyranosido-*D*-fructose, the probable relationship of turanose to maltose, and the possible relationship of laminaribiose to cellobiose. H. W.

Separation of methylated sugars by chromatographic adsorption of their azobenzene-4-carboxylates. J. K. Mertzweiler, D. M. Carney, and F. F. Farley (*J. Amer. Chem. Soc.*, 1943, **65**, 2367—2368).—*p*-$PhN_2{\cdot}C_6H_4{\cdot}CO$ esters of methylated sugars are prepared in C_5H_5N at, successively, 0° (3 days), 30° (2 days), and 0° (3 days) and are purified by dissolution in $CHCl_3$ and then filtration through a 4—5-cm. column of Al_2O_3 (to remove *p*-$PhN_2{\cdot}C_6H_4{\cdot}CO_2H$), and finally crystallisation from $CHCl_3$–EtOH or EtOH. Yields are ≮95%. Mixed esters are separated by chromatography (? from $CHCl_3$–C_6H_6–light petroleum) on SiO_2 (prep. described); elution is by 1 : 4 EtOH–$CHCl_3$; the solutions obtained are examined colorimetrically as they contain colloidal SiO_2. Excellent results are described for mixed esters of (i) 2 : 3 : 4 : 6-tetramethyl- (I) and 3-methyl-glucose and (ii) (I), 2 : 3 : 6-tri- and 2 : 3-di-methylglucose. R. S. C.

Constitution and configuration of digitalose. O. T. Schmidt, W. Mayer, and A. Distelmaier [with, in part, E. Fürst] (*Annalen*, 1943, **555**, 26—41, and *Naturwiss.*, 1943, **31**, 247—248; cf. Kiliani, A., 1931, 1273).—Digitalose (I) is 3-*methyl*-d-*fucose* (*A*). Digitalin is hydrolysed and the product is largely freed from glucose by fermentation with brewer's yeast. The resulting (I) after crystallisation from EtOH is 80% pure according to OMe content and with $NHPh{\cdot}NH_2$ in aq. AcOH at 100° gives *digitalosephenylosazone*, m.p. 179—180°, $[\alpha]_D^{\alpha}$ +0·5° to +18° (final val.) in C_5H_5N–EtOH (2 : 3). OMe in (I) cannot therefore be attached to $C_{(2)}$. Attachment at $C_{(5)}$ is also excluded since digitalonic acid is oxidised by HNO_3 to a trihydroxyglutaric acid which contains the first 5 C atoms of (I) and also OMe. Since digitalonolactone, m.p. 137—138°, $[\alpha]_D^{20}$ −92·5° to −74·9° in H_2O in 16 days, has the γ structure OMe is not united to $C_{(5)}$ and only $C_{(3)}$ remains. α-Methyl-*l*-fucoside is converted by 10N-NaOH and Me_2SO_4 into 2 : 3 : 4-*trimethyl-α-methyl*-l-*fucoside*, b.p. 84—88°/1 mm., m.p. 97—98°, $[\alpha]_D^{20}$ −209°±1° in H_2O. 2 : 3 : 4-*Trimethyl-β-methyl*-l-*fucoside*, b.p. 82—84°/1 mm., m.p. 101·5—102·5°, $[\alpha]_D^{\alpha}$ −21·1°±1° in H_2O, is obtained analogously. These are hydrolysed



by N-H_2SO_4 at 85° to 2 : 3 : 4-*trimethyl*-α-l-*fucose* (**II**), m.p. 36—37°, $[\alpha]_D^{20}$ −130°±1·3° (final val.) in H_2O {*monohydrate*, m.p. 65°, $[\alpha]_D^{20}$ −169°±2° to −118°±2° (final val.) in H_2O}. (**I**) is transformed by HCl–MeOH into a mixture of α- and β-methyldigitaloside, further methylated by K and MeI in liquid NH_3 to a mixture of trimethylmethyldigitalosides. This is hydrolysed by N-H_2SO_4 at 85° and the product is distilled and finally crystallised from Et_2O–light petroleum, thus giving 2 : 3 : 4-*trimethyl*-α-d-*fucose monohydrate*, m.p. 65°, $[\alpha]_D^{20}$ +168·6°±2° to +118°±2° (final val. after 24 hr.) in H_2O; this is the optical antipode of (**II**). β-Methyl-*l*-fucoside is converted by $COMe_2$ containing conc. H_2SO_4 into 3 : 4-iso*propylidene*-β-*methyl*-l-*fucoside* (+1H_2O), m.p. (indef.) 89—97°, transformed by Na and MeI in Et_2O into 2-*methyl*-3 : 4-iso*propylidene*-β-*methyl*-l-*fucoside* (+1H_2O), m.p. 88—92°, $[\alpha]_D^{20}$ −10·9°±1° in MeOH. *l*-Fucose, from *Fucus vesiculosus*, is converted by $CH_2Ph{\cdot}SH$ and saturated HCl at −15° into l-*fucose dibenzyl mercaptal*, m.p. 184°, $[\alpha]_D^{20}$ +27·8° in C_5H_5N. *l*-Fuconamide, m.p. 182°, is converted by NaOCl and NaOH into *l*-lyxomethylose, isolated as the *phenylbenzylhydrazone*, m.p. 100·5—101°, $[\alpha]_D^{20}$ −36·4° in C_5H_5N. H. W.

Photolysis of the *d*-glycosides : α-benzylfructofuranoside, β-benzylfructopyranoside, and α- and β-phenyl-, -benzyl-, and β-phenylethylglucosides ; and the bearing of the data on the transfer of energy between molecules.—See A., 1944, I, 132.

β-β′β′β′-Trichloroethylgentiobioside, m.p. 204—206° (decomp.), $[\alpha]_D^5$ −41·2° in H_2O.—See A., 1944, III, 384.

Polysaccharide hydroxylation by means of *p*-toluenesulphonyl chloride and triphenylchloromethane. W. Low and E. V. White (*J. Amer. Chem. Soc.*, 1943, **65**, 2430—2432).—The arabogalactan (**I**) from *Larix occidentalis* with *p*-$C_6H_4Me{\cdot}SO_2Cl$ in C_5H_5N at 55—90° (1–38 hr.) and then NaI–$COMe_2$ at 100° gives a product in which, independently of the *p*-$C_6H_4Me{\cdot}SO_2$ content (4·7—13·1 units), 3·08—3·21 $C_6H_4Me{\cdot}SO_2$ are replaced and 2·93—3·22 I are introduced. With CPh_3Cl in C_5H_5N at 50° (**I**) gives a product containing 2·80 CPh_3, into which Ac_2O–C_5H_5N introduces 15·6 Ac (CPh_3 : Ac = 3 : 17·2). Thus (**I**) is proved to contain 3 primary OH. R. S. C.

Structure of pyrodextrins. B. Brimhall (*Ind. Eng. Chem.*, 1944, 36, 72—75).—A roasted maize-starch product of British gum type yielded 70% of a fraction (*F*), sol. in 30% and insol. in 70% MeOH, which behaved towards HIO_4 similarly to starch and contained no linear mols. of sufficient length to give a blue I colour, though the average mol. size was ~66 glucose units. Solubility relationships indicated a structure different from that of acid-produced amylodextrins (*A*), whilst *F* was degraded only to the extent of 22% by β-amylase and gave no Schardinger dextrins with *B. macerans*. End-group assay in conjunction with mol. size indicated for *F* a mol. with 4—5 branches with ~5 glucose units in each. Dextrination of amylopectin, amylose, *A*, and other starch products, followed by changes in solubility, reducing power, and β-amylase digestibility, shows that heating causes linear portions of starch mols. to become branched, and the probable mechanism of this change is discussed. I. A. P.

Cellulose triphenylmethyl ether. W. M. Hearson, G. D. Hiatt, and C. R. Fordyce (*J. Amer. Chem. Soc.*, 1943, **65**, 2449—2452).—Cellulose (best, regenerated from the acetate) and CPh_3Cl in C_5H_5N give an ether [1·03 CPh_3 (in this and similar cases per glucose unit)], which with PhNCO–C_5H_5N gives a CPh_3 ether phenylcarbamate (1·03 CPh_3, 1·97 NHPh·CO). HCl–dioxan removes all the CPh_3, giving an ester (1·97 NHPh·CO), which with *p*-$C_6H_4Me{\cdot}SO_2Cl$–C_5H_5N yields a mixed ester (1·97 NHPh·CO, 0·95 *p*-$C_6H_4Me{\cdot}SO_2$), converted by NaI in $COMe_2$ into a product containing 1·97 NHPh·CO, 0·90 I, and 0·05 *p*-$C_6H_4Me{\cdot}SO_2$. Thus, of the 1·03 CPh_3 introduced, 0·90 were attached to primary and 0·13 to *sec.* OH; the relative reactivities are thence calc. to be 13·8 : 1. The optimum conditions for the reactions described are reported. R. S. C.

III.—HOMOCYCLIC.

Transformations of hydrocarbons at a vanadium contact. III. Ethyl*cyclo*pentane. A. F. Plate and O. G. Sterligov (*J. Gen. Chem. Russ.*, 1943, **13**, 202—212).—Ethyl*cyclo*pentane passed over 1 : 10 V_2O_5–Al_2O_3 catalyst at 440—500° yields gaseous (H_2, C_nH_{2n+2}, C_nH_{2n}, CO, CO_2) and liquid products (methyl*cyclo*pentadiene, *cyclo*pentadiene, PhMe). The catalyst is gradually inactivated by a layer of soot; it may be reactivated by passing air at 500°. R. T.

Semicyclic ethylenic linkings. Effect of certain reagents capable of addition to ethylenic linkings on *cyclo*hexylidene derivatives. D. N. Kursanov and A. S. Kursanova (*J. Gen. Chem. Russ.*, 1943, **13**, 184—188).—The C:C linking of *cyclo*hexylideneacetic acid (**I**) does not react with *cyclo*pentadiene under the conditions of the Diels–Alder diene reaction. The Me ester (**II**) of (**I**) with MgMeI yields γ-cyclo*hexylidene*-β-*methyl*-Δ$^{\alpha}$-*propene*, b.p. 103—103·5°/62 mm., which does not react with $CH_2{:}CH{\cdot}CHO$. (**II**) does not react with CH_2N_2 or with $CHN_2{\cdot}CO_2Et$. It is concluded that the reactivity of semicyclic C:C linkings is < of those in other positions. R. T.

New type of carotene pigment from red yeast (*Torula rubra*).—See A., 1944, III, 369.

3-Chloro-1-α-chlorovinyl-Δ^3-*cyclo*hexene and 1 : 5-dichloro-Δ$^{1:5}$-*cyclo*octadiene. J. G. T. Brown, J. D. Rose, and J. L. Simonsen (*J.C.S.*, 1944, 101—103).—The two dimerides formed when chloroprene is kept (cf. Carothers *et al.*, B., 1932, 156; A., 1933, 371) are shown to be 3-*chloro*-1-α-*chlorovinyl*-Δ^3-cyclo*hexene* (**I**), b.p. 66—67°/4 mm., 105°/20 mm., and 1 : 5-*dichloro*-Δ$^{1:5}$-cyclo*octadiene* (**II**), b.p. 84—85°/2 mm., 126°/18 mm., by the reactions below. With Br (**I**) gives a *tetrabromide*, m.p. 146—147°. (**I**) on hydrogenation gives ethyl*cyclo*hexane, and on ozonolysis gives β-α-*chlorovinyladipic acid* (**III**), m.p. 152—154° (*di*-p-*phenylphenacyl ester*, m.p. 54—55°). (**III**) on ozonolysis gives butane-αβδ-tricarboxylic acid, m.p. 121—122°. Hydrogenation of (**III**) (Pd catalyst) gives β-*ethyladipic acid* (**IV**), m.p. 47—49° (*di*-p-*phenylphenacyl ester*, m.p. 100—101°). Reduction of *Et* 1-*ethyl*cyclo*pentan*-2-*one*-1-*carboxylate*, b.p. 115°/13 mm. (from Et sodio*cyclo*pentan-2-one-1-carboxylate and EtI), gives *Et* α-*ethyladipate* (**V**), b.p. 133°/13 mm. (**V**) gives α-ethyladipic acid, m.p. 47—49° (*di*-p-*phenylphenacyl ester*, m.p. 118—120°), not identical with (**IV**). Hydrogenation of (**II**) (PtO_2 catalyst) gives *cyclo*octane, which yields suberic acid, m.p. 140—141°, on oxidation. Ozonolysis of (**II**) gives $(CH_2{\cdot}CO_2H)_2$ and a CHO-acid, probably δ-*chloro*-η-*carboxy*-Δ$^{\delta}$-*heptenal*, isolated as its 2 : 4-dinitrophenylhydrazone, m.p. 119°. D. G.

Cyclic compounds containing sulphur. M. Mousseron (*Compt. rend.*, 1942, **215**, 357—359).—Na_2S and 2-chloro*cyclo*hexanol at ~70° yield *di*-2-*hydroxy*cyclo*hexyl sulphide* (**I**), b.p. 215°/20 mm., m.p. 71—72° (*diacetate*, m.p. 61—62°), whereas under the same conditions or in the cold epoxy*cyclo*hexane affords (**I**) with a small proportion of an *isomeride* (**II**), m.p. 89°. (**I**) and (**II**) are regarded as *dl*- and *meso*-forms. *cis*-2-Chloro*cyclo*hexanol gives the cis-cis-*di*-2-*hydroxy*cyclo*hexyl sulphide*, m.p. 103—104°. *Di*-2-*hydroxy*-cyclo*pentyl*, b.p. 205°/20 mm., m.p. 44°, -cyclo*heptyl*, b.p. 225°/20 mm., m.p. 88°, *di*-3-*hydroxy*-1 : 2 : 3 : 4-*tetrahydro*-2-*naphthyl*, m.p. 151°, and *di*-3-*hydroxy*-2 : 3-*dihydro*-2-*indenyl*, m.p. 135°, *sulphide* are described. A similar change does not appear to occur with 4-chloro-*cyclo*hexanol. The action of NaCNS and anhyd. $CuSO_4$ on cyclenes affords 1 : 2-dithiocyano-2-methyl-, m.p. 60°, -*ethyl*-, m.p. 82°, -*propyl*-, m.p. 86°, and -4-*methyl*-, m.p. 81°, -cyclo*hexane*, 1-*thiocyano*-2-*thiocyanomethyl*cyclo*hexane*, m.p. 63°, 2 : 3-*dithiocyano*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 113°, and 2 : 3-*dithiocyanodecahydronaphthalene*, m.p. 74°. Optically active 1-methyl-Δ^3-*cyclo*hexene adds NH_4HSO_3 to give NH_4 3-methyl*cyclo*hexanesulphonate, characterised by the *Ba* salt, $[\alpha]_{5461}$ +4·38° in H_2O, and the optically inactive NH_4 4-*methyl*cyclo*hexanesulphonate*. 2-Chloro*cyclo*hexanone and NaSEt in anhyd. Et_2O afford cyclo*pentanethiocarboxylic acid*, b.p. 103°/15 mm., m.p. 92—93°. H. W.

Reductions with nickel–aluminium alloy and aqueous alkali. II. Displacement of groups by hydrogen. E. Schwenk, D. Papa, B. Whitman, and H. Ginsberg (*J. Org. Chem.*, 1944, **9**, 1—8; cf. A., 1943, II, 93).—When treated with Ni–Al alloy and aq. alkali halogens and SO_3H are displaced by H, the reaction being apparently independent of their no. or position or of the presence of other groups {substances tested are PhBr, *m*-$C_6H_4Cl{\cdot}CO_2H$, *p*-$C_6H_4Cl{\cdot}NO_2$, *p*-$C_6H_4Cl{\cdot}CHO$, 2 : 5 : 1-$OH{\cdot}C_6H_3Cl{\cdot}CHO$, *p*-$C_6H_4Br{\cdot}COMe$, *p*-$C_6H_4Cl{\cdot}CO{\cdot}[CH_2]_2{\cdot}CO_2H$, $PhSO_3H$, *o*- and *m*-$SO_3H{\cdot}C_6H_4{\cdot}CO_2H$, 2-$C_{10}H_7{\cdot}SO_3H$, 2 : 6-$OH{\cdot}C_{10}H_6{\cdot}SO_3H$, and 2 : 3 : 6-$OH{\cdot}C_6H_5(SO_3H)_2$}. All halogen compounds exchange halogen for H quantitatively. Arsanilic acid and HgPh·OAc yield NH_2Ph and Ph_2 respectively. Only halogen and SO_3H are displaced by H from monosubstituted derivatives of C_6H_6. *o*-$NH_2{\cdot}C_6H_4{\cdot}OMe$ and *o*-, *m*-, and *p*-$C_6H_4Me{\cdot}OMe$ are unchanged, but when the *o*–*p*-directive Me or NH_2 of these compounds is replaced by *m*-directive CO_2H quant. replacement of OMe occurs from *o*- and *p*-$OMe{\cdot}C_6H_4{\cdot}CO_2H$ whereas *m*-$OMe{\cdot}C_6H_4{\cdot}CO_2H$ remains unaffected. The displacement of OMe from the *m*-position has not yet been observed. A similar displacement of OMe ocurs with other *m*-directive groups such as NO_2, CHO, and Ac. These groups are themselves reducible to the *o*–*p*-orienting NH_2 or Alk. Elimination of OMe can occur only before these groups are reduced. Therefore *p*-$NO_2{\cdot}C_6H_4{\cdot}OMe$ gives NH_2Ph as first change and *p*-$NH_2{\cdot}C_6H_4{\cdot}OMe$ as product of reaction after reduction of NO_2 to NH_2. The two possible reduction products are also obtained from *p*-$OMe{\cdot}C_6H_4{\cdot}CH_2{\cdot}OH$ and *o*- and *p*-$OMe{\cdot}C_6H_4{\cdot}CHO$ with in some cases BzOH, probably resulting from a Cannizzaro change in the alkaline medium. Similar loss of alkoxy-groups occurs with *p*-$OEt{\cdot}C_6H_4{\cdot}CHO$, *o*-$OEt{\cdot}C_6H_4{\cdot}CO_2H$, *p*-$OPr^{\alpha}{\cdot}C_6H_4{\cdot}CO_2H$, *p*-$OPr^{\beta}{\cdot}C_6H_4{\cdot}CO_2H$, and *p*-$OBu{\cdot}C_6H_4{\cdot}CO_2H$. *o*-$CH_2Ph{\cdot}O{\cdot}C_6H_4{\cdot}CO_2H$ affords PhMe and *o*-$OH{\cdot}C_6H_4{\cdot}CO_2H$ but *o*-$SMe{\cdot}C_6H_4{\cdot}CO_2H$ gives only BzOH. Introduction of OH or OMe as third group in the disubstituted derivatives of C_6H_6 alters considerably the course of the displacement since in many cases removal of *m*-orienting groups is observed. In the trisubstituted products 4 : 1 : 3-$OH{\cdot}C_6H_3R{\cdot}OMe$ (R = $\cdot CH_2{\cdot}OH$, CHO, or Ac), 3 : 2 : 1- and 3 : 4 : 1-$OH{\cdot}C_6H_3(OMe){\cdot}CHO$, 3 : 2 : 1-, 4 : 3 : 1-, and 4 : 2 : 1-$(OMe)_2C_6H_3{\cdot}CHO$ displacement of CHO by H occurs; the only products isolated are *o*-$OH{\cdot}C_6H_4{\cdot}OMe$ or $C_6H_4(OMe)_2$. 4 : 3 : 1-$OH{\cdot}C_6H_3(OMe){\cdot}CO_2H$ is recovered unchanged whereas 3 : 4 : 1-$OH{\cdot}C_6H_3(OMe){\cdot}CO_2H$ affords *m*-$OH{\cdot}C_6H_4{\cdot}CO_2H$ if a greatly

increased proportion of alloy and alkali is used. OMe is not displaced from 3 : 2 : 1-, 4 : 3 : 1-, or 4 : 2 : 1-$(OMe)_2C_6H_3\cdot CO_2H$. 3 : 4 : 1-$(OMe)_2C_6H_3\cdot CO\cdot[CH_2]_2\cdot CO_2H$ (I) does not lose 4-OMe although *p*-$OMe\cdot C_6H_4\cdot CO\cdot[CH_2]\cdot CO_2H$ gives $Ph\cdot[CH_2]_3\cdot CO_2H$ in 65% yield; (I) affords γ-3 : 4-dimethoxyphenylbutyrolactone in 70% yield with a small amount of intractable oil. Neither CO_2H nor OMe is displaced from 3 : 4 : 5 : 1-$(OMe)_3C_6H_2\cdot CO_2H$. H. W.

Polymorphic and isomorphic phenomena with trinitrotoluene etc. —See A., 1944, I, 100.

Ethylation of benzene. Course of the reaction. E. M. Marks, J. M. Almand, and E. E. Reid (*J. Org. Chem.*, 1944, **9**, 13—20).—The proportions of the products obtained by the action of C_2H_4 on C_6H_6 in the presence of $AlCl_3$ depend greatly on the rate of passage of the gas, the temp., the rate of stirring, and the amount of catalyst. A portion of the C_6H_6 appears to be transformed into C_6Et_6, which is then dealkylated to a type of equilibrium mixture containing much *s*-$C_6H_3Et_3$. H. W.

Poly*iso*propylbenzenes. III. Sulphonyl and nitrosulphonyl chlorides. A. Newton (*J. Amer. Chem. Soc.*, 1943, **65**, 2439—2441).—Susceptibility to replacement of Pr^β on treatment of poly*iso*propylbenzenes with $ClSO_3H$ (3 equivs.) in CCl_4 at 30—32° (rising to 45—55°) is sometimes more marked than in nitration. *m*-$C_6H_4Pr^\beta_2$ gives 1 : 3 : 4-$C_6H_3Pr^\beta_2\cdot SO_2Cl$ (I), m.p. 35—40° (derived *amide*, m.p. 144·2—144·9°, and *anilide*, m.p. 113·9—114·5°). *p*-$C_6H_4Pr^\beta_2$ gives p-*di*iso*propylbenzene*-2-*sulphonyl chloride* (II), m.p. 52·5—53° (derived *amide*, m.p. 110·2—110·8°, and *anilide*, m.p. 124·1—125°). 1 : 2 : 4-$C_6H_3Pr^\beta_3$ gives 1 : 2 : 4-*tri*iso*propylbenzene*-5-*sulphonyl chloride* (III), m.p. 141·5—142·2° (derived *amide*, m.p. 154·8—155·7°, and *anilide*, m.p. 187·8—188·8°). *s*-$C_6H_3Pr^\beta_3$ gives 1 : 3 : 5-*tri*iso*propylbenzene*-2-*sulphonyl chloride* (IV), m.p. 97·2—98·4° (derived *amide*, m.p. 119·0—129·6°, and *anilide*, m.p. 163·6—164·2°). 1 : 2 : 4 : 5-$C_6H_2Pr^\beta_4$ gives (III) (incorrectly described by Huntress *et al.*, A., 1942, II, 136, as 1 : 2 : 4 : 5 : 3-$C_6HPr^\beta_4\cdot SO_3Cl$). With an excess of 96% HNO_3, (I) or (III) gives 6-*nitro*-1 : 3-*di*iso*propylbenzene*-4-*sulphonyl chloride*, m.p. 102·1—103° (derived *amide*, m.p. 192·4—192·8°, and *anilide*, m.p. 169·8—170·6°), (II) gives 4-*nitro*-1-iso*propylbenzene*-2-*sulphonyl chloride*, m.p. 101·6—102·1° (derived *amide*, m.p. 172·5—173·5°, and *anilide*, m.p. 192·8—193·7°), and (IV) gives 4-*nitro*-1 : 3 : 5-*tri*iso*propylbenzene*-2-*sulphonyl chloride* (V), m.p. 157·5—158° (derived *amide*, m.p. 165·9—166·3°, and *anilide*, m.p. 182·4—183·3°); these NO_2-products can be purified only by chromatography (Al_2O_3); 4% of a *dinitrohexa*iso*propyldiphenyl sulphone*, m.p. 150·2—151·1°, is isolated from crude (V).

R. S. C.

Nitration of halogenodiphenyls. II. Di- and tetra-nitro-derivatives of 2 : 2′-dichlorodiphenyl. F. H. Case and R. U. Schock, jun. **III. Nitro-derivatives of 2-chloro- and 2-bromodiphenyl.** F. H. Case (*J. Amer. Chem. Soc.*, 1943, **65**, 2086—2088, 2137—2140; cf. A., 1943, II, 26).—II. $(o\text{-}C_6H_4Cl)_2$ (I) with conc. HNO_3–H_2SO_4 at <40° and then 100° gives 2 : 2′-dichloro-5 : 5′- (II), m.p. 202—203° [also obtained (m.p. 203—204°) from 5 : 2 : 1-$NO_2\cdot C_6H_4Cl$ (III) by Cu], with a small amount of 2 : 2′-*dichloro*-3 : 3′-(? 3 : 5′-)*dinitrodiphenyl* (IV), m.p. 128—129° (cf. Mascarelli *et al.*, A., 1934, 62). With HNO_3 (*d* 1·6)–H_2SO_4 at 100°, (I), (II), or (IV) gives 2 : 2′-*dichloro*-3 : 3′ : 5 : 5′-*tetranitrodiphenyl* (V), m.p. 304—305°, which loses its Cl to $NaNO_2$ in 50% aq. dioxan (to give a non-phenolic product) (cf. van Alphen, A., 1932, 729). 2-*Chloro*-1-*iodo*-4 : 6-*dinitrobenzene* [prep. from 4 : 6 : 2 : 1-$(NO_2)_2C_6H_2Cl\cdot NH_2$], m.p. 117—118°, with Cu at 240° gives 2 : 2′-*dichloro*-4 : 4′ : 6 : 6′-*tetranitrodiphenyl*, m.p. 159—160°. 2 : 1 : 4-$C_6H_3ClI\cdot NO_2$ and Cu give 2 : 2′-*dichloro*-4 : 4′-*di*-, m.p. 107—108°, and thence 2 : 2′-*dichloro*-4 : 5 : 4′ : 5′-*tetranitrodiphenyl* (VI), m.p. 201—202°. With H_2SO_4–HNO_3 (*d* 1·6) at 100° (III) gives 2-*chloro*-1-*iodo*-4 : 5-*dinitrobenzene*, m.p. 98—99°, which with Cu powder in boiling $PhNO_2$ gives (VI). 2-*Iodo*-4 : 6-*dinitroanisole* (prep. from the phenol by CH_2N_2), m.p. 69—70°, with Cu powder in boiling $PhNO_2$ gives [2 : 3 : 5 : 1-$OMe\cdot C_6H_2(NO_2)_2]_2$, m.p. 186—187° [also obtained from $(o\text{-}OMe\cdot C_6H_4)_2$], and thence by hydrolysis [2 : 3 : 5 : 1-$OH\cdot C_6H_2(NO_2)_2]_2$ (VII), m.p. 245—246° (lit. 249—250°) (cf. Diels *et al.*, A., 1902, i, 219; Borsche *et al.*, A., 1917, i, 390). The structure of (V) is proved by conversion into (VII) by $NaNO_2$ in boiling aq. dioxan.

III. The structure of *o*-$C_6H_4Cl\cdot C_6H_4\cdot NO_2$-*p* (VIII), m.p. 74—75°, of Mascarelli *et al.* (*loc. cit.*) is confirmed by prep. from *p*-$NO_2\cdot C_6H_4\cdot C_6H_4\cdot NH_2$-*o* by a Sandmeyer reaction, but the compound, m.p. 159—160°, supposed (*loc. cit.*) to be *o*-$C_6H_4Cl\cdot C_6H_3(NO_2)_2$-1 : 3 : 4, is 2-*chloro*-4′ : 5-*dinitrodiphenyl* (IX). (IX) is obtained by nitrating (VIII) (proof of the 4′-NO_2), is unchanged by boiling CrO_3–V_2O_5–AcOH, and is destroyed by reduction. 5 : 2 : 1-$NO_2\cdot C_6H_4Cl\cdot N_2Cl$ in 1 : 1 conc. HCl–H_2O with C_6H_6 and 5N-NaOH gives 2-*chloro*-5-*nitrodiphenyl*, m.p. 59—60°, which with HNO_3 (*d* 1·5) at 100° gives (IX) (proof of the 5-NO_2). By Schoutissen's method 2 : 4 : 1-$NH_2\cdot C_6H_3(NO_2)\cdot C_6H_4\cdot NO_2$-*p* gives 2-*chloro*-4 : 4′-*dinitrodiphenyl*, m.p. 153—154°. *o*-C_6H_4PhBr with, best, $OEt\cdot NO_2$ in conc. H_2SO_4 at <2° and then 25° gives 2-bromo-4′ : 5- (X), m.p 165—166° (Finzi *et al.*, A., 1938, II, 225), and some -2′ : 5-*dinitrodiphenyl* (XI), m.p. 139—140° [also obtained (m.p. 140—141°) similarly from *o*-$C_6H_4Br\cdot C_6H_4\cdot NO_2$-*o*]. 5 : 1 : 2-$NO_2\cdot C_6H_3Ph\cdot NH_2$ (prep. from the *p*-$C_6H_4Me\cdot SO_2$ derivative by boiling 1 : 1 H_2SO_4), m.p. 125—126°, in AcOH with $NaNO_2$–H_2SO_4 at <40° and then CuBr in H_2O–HBr gives 1 : 2 : 5-$C_6H_3PhBr\cdot NO_2$ (XII) and thence (HNO_3–H_2SO_4) (X). 2-*Bromo*-4 : 4′-*dinitrodiphenyl*, m.p. 148—149°, is similarly prepared. *o*-$C_6H_4Br\cdot C_6H_4\cdot NH_2$-*p* with KNO_3 in H_2SO_4–oleum at <6° and then Ac_2O gives 2-*bromo*-5-*nitro*-4′-*acetamido*-, m.p. 186—187°, hydrolysed by boiling H_2SO_4–H_2O to 2-*bromo*-5-*nitro*-4′-*aminodiphenyl* (XIII), m.p. 111—112°, which with $NaNO_2$ in EtOH–dil. H_2SO_4 gives (XII). KNO_3–H_2SO_4–oleum converts (XIII) into 2-*bromo*-2′ : 5-*dinitro*-4′-*aminodiphenyl*, m.p. 149—150° (isolated as *Ac* derivative, m.p. 246—247°), whence (XI) is obtained by deamination. HNO_3 (*d* 1·59) at 100° converts (X) or (XI) into 2-*bromo*-5 : 2′ : 4′-*trinitrodiphenyl*, m.p. 140—141°. *o*-$C_6H_3Br\cdot C_6H_4\cdot NHAc$-*p* and HNO_3 (*d* 1·5) in Ac_2O–AcOH at 70° give 2-*bromo*-3′-*nitro*-4′-*acetamido*-, m.p. 135—136° and thence -4′-*amino*-*diphenyl*, m.p. 145—146°, which with $NaNO_2$–H_2SO_4–H_2O–EtOH gives *o*-$C_6H_4Br\cdot C_6H_4\cdot NO_2$-*m*, m.p. 79—80°. With $OEt\cdot NO_2$ this gives 2-*bromo*-5 : 3′-*dinitrodiphenyl* (XIV), m.p. 165—166°, which with boiling $SnCl_2$–EtOH and then Ac_2O gives 2-*bromo*-5 : 3′-*diacetamidodiphenyl* (XV), m.p. 265—266°. *m*-$NO_2\cdot C_6H_4\cdot C_6H_4\cdot NHAc$-*m* with Br in AcOH–NaOAc gives 2-*bromo*-3′-*nitro*-5-*acetamidodiphenyl* (XVI), m.p. 193—194°, and thence the 5-NH_2-compound, m.p. 112—113°, which yields, as above, 2 : 5-*dibromo*-3′-*nitrodiphenyl*, m.p. 97—98°, converted by $SnCl_2$–EtOH and then CrO_3–AcOH into 2 : 5 : 1-$C_6H_3Br\cdot CO_2H$. $SnCl_2$–EtOH reduces (XVI) to (XV). 5 : 2 : 1-$NO_2\cdot C_6H_3Br\cdot N_2\cdot HSO_4$ in AcOH–H_2SO_4 is converted by KI–NaOAc–H_2O at 0° into 4-*bromo*-3-*iodo*-1-*nitrobenzene*, m.p. 97—98°, which with 1 : 3 : 4-$C_6H_3I(NO_2)_2$ and Cu gives 2-*bromo*-5 : 3′ : 4′-*trinitrodiphenyl*, m.p. 222—223°, also obtained from (XIV) by HNO_3 (*d* 1·59) and oxidised by CrO_3–V_2O_5–AcOH to 5 : 2 : 1-$NO_2\cdot C_6H_3Br\cdot CO_2H$.

R. S. C.

Use of semi-micro-technique in elementary organic chemistry. IV. Semi-micro-chlorination of organic compounds. N. D. Cheronis (*J. Chem. Educ.*, 1943, **20**, 611—614, 621).—Apparatus for, and results obtained in, the semi-micro-chlorination of C_6H_6, PhMe, $C_{10}H_8$, and *cyclo*hexane are described. L. S. T.

Xanthhydrol as a reagent for the identification of sulphonamides. R. F. Phillips and V. S. Frank (*J. Org. Chem.*, 1944, **9**, 9—12).—Unsubstituted sulphonamides condense with xanthhydrol in AcOH at room temp. to N-*xanthylsulphonamides*, $SO_2R\cdot NH\cdot CH(C_6H_4)_2O$, which are dried at room temp. and crystallised from dioxan–H_2O (3 : 1). Thus are obtained *benzenesulphonxanthylamide*, m.p. 200—200·5° (block), and the following derivatives: o-*Me*, m.p. 182—183·5°, p-*Me*, m.p. 197—197·5°, p-*Et*, m.p. 195·5—197°, p-Pr^n, m.p. 199—200·5°; p-Bu^n, m.p. 185—186·5°, p-n-*amyl*, m.p. 164·5—165°; 3 : 4-Me_2, m.p. 189—190°, 2 : 4-Me_2, m.p. 187—188·5°; 2 : 5-Me_2, m.p. 175—176°; 2 : 4 : 6-Me_3, m.p. 203—204°; p-NH_2-, m.p. 207—208°, and *saccharin*-, m.p. 198—199°. Xanthyl derivatives are not obtained from 2 : 4 : 6 : 1-$C_6H_2Et_3\cdot SO_2\cdot NH_2$, *p-tert.*-butyl-, *p-tert.*-amyl-, and the *p*-cymene-benzenesulphonamides and *p*-$C_6H_4Me\cdot NEt\cdot SO_2H$. *p-sec.*-Butyl- and 2-methyl-4-*iso*propylbenzenesulphonamides give very poor yields of products. Branched alkyl groups appear to inhibit the reaction and larger *N*-alkyl groups retard its rate. (See also C., 1944, 86.) H. W.

Organic reactions with boron fluoride. XXIX. Sulphonation of naphthalene derivatives in presence of boron trifluoride. G. F. Hennion and C. J. Schmidle (*J. Amer. Chem. Soc.*, 1943, **65**, 2468—2469; cf. A., 1944, II, 10).—BF_3 acts in sulphonation reactions only as a powerful dehydrating agent and has no orienting influence. Passing BF_3 into α-$C_{10}H_7\cdot NH_2$ in H_2SO_4 at 75—80° gives 86% of $NH_2\cdot C_{10}H_6\cdot SO_3H$, the yield being 60% in absence of BF_3. Similarly, at 50—55° β-$C_{10}H_7\cdot NH_2$ gives 95% of acids containing 52% of 2 : 5- and 48% of 2 : 8-$NH_2\cdot C_{10}H_7\cdot SO_3H$; at 20 these proportions are 44 : 56 and at 80° are 67 : 33; in absence of BF_3 only 57% sulphonation occurs. Passing BF_3 into β-$C_{10}H_7\cdot OH$ (29 g.) in H_2SO_4 (previously saturated with BF_3 at room temp.) at 80—90° gives 22 g. of acid, mainly 2 : 3 : 6-$OH\cdot C_{10}H_5(SO_3H)_2$.

R. S. C.

Poly*iso*propylbenzenes. II. Nitro- and amino-derivatives. A. Newton (*J. Amer. Chem. Soc.*, 1943, **65**, 2434—2439; cf. A., 1943, II, 222).—Nitration of poly*iso*propylbenzenes usually, but not always, involves partial replacement of Pr^β by NO_2 when all the orienting groups favour entry of NO_2 at this position. In absence of this condition, no such replacement occurs. In experiments recorded below, hydrocarbons were nitrated by 96% HNO_3 (1·24 2·05 mols.) in AcOH–Ac_2O at 45—50° and then usually kept at room temp. for 24 hr.; NO_2-compounds (2·5 g.) were oxidised by 70% HNO_3 (20 ml.) and H_2O (12 ml.) at 180° (H_2), yields of crude acids being 50—60% for NO_2- and 13% for $(NO_2)_2$-compounds; NO_2-compounds were reduced to amines by H_2–Raney Ni in 99% $Pr^\beta OH$ at 100°/1200 lb.; amines were nitrated in H_2SO_4 by 70% HNO_3 (1·1 mols.) at 5—10°. *m*-$C_6H_4Pr^\beta_2$ gives a 95% yield of 2- (25%) and 4-*nitro*-m-*di*iso*propylbenzene* (74%) (and traces of polynitro-compounds), oxidised to 2 : 1 : 3- and 4 : 1 : 3-$NO_2\cdot C_6H_3(CO_2H)_2$, respectively, and reduced to 2-, an oil (*Bz*, m.p. 106—106·7°, and ? Ac_2 derivative, an oil), and 4-*amino*-m-*di*iso*propylbenzene* (I) (*Ac*, m.p. 108·3—109°, and *Bz* derivative, m.p.

162·8—163·4°), respectively. With 96% HNO_3 (3·17 mols.) in H_2SO_4 at 70°, *m*-$C_6H_4Pr^{\beta}_2$ gives 4 : 6-*dinitro*-m-*diiso*propylbenzene, m.p. 76·9—77·7°, oxidised to 4 : 6 : 1 : 3-$(NO_2)_2C_6H_2(CO_2H)_2$ (Et_2 ester, new m.p. 124·5—125·2°) and reduced (one NO_2 at room temp., the other at 60°) to 4 : 6-*diamino*-m-*diiso*propylbenzene (II), m.p. 72·6—72·9° [Ac_2 derivative, m.p. 320·5—321·5° (uncorr.)]. (I) gives 6-*nitro*-4-*amino*-m-*diiso*propylbenzene (III), m.p. 75·3—76·1° (*Ac* derivative, m.p. 116·2—117°), and thence (II). By the general method, *p*-$C_6H_4Pr^{\beta}_2$ gives *p*-$C_6H_4Pr^{\beta}\cdot NO_2$ (49·7%) and 2-*nitro*-p-*diiso*propylbenzene (33·7%), yields being 65·0 and 13·6%, respectively, when 70% HNO_3 (~2 mols.) in H_2SO_4 at 0—6° is used. Reduction then affords *p*-$C_6H_4Pr^{\beta}\cdot NH_2$ (*hydrochloride*; Ac, new m.p. 105·8—106·6°, and Bz derivative, m.p. 161·4—162°), and 2-*amino*- (*hydrochloride*; *Ac*, m.p. 80·8—81·5°, and *Bz* derivative, m.p. 124·6—125°), and thence 6-*nitro*-2-*amino*-, m.p. 95·2—96·3°; and 2 : 6-*diamino*-p-*diiso*propylbenzene, m.p. 77·9—78·3°. 1 : 2 : 4-$C_6H_3Pr^{\beta}_3$ gives 5-*nitro*- and thence 5-*amino*-1 : 2 : 4-*tri*-*iso*propylbenzene-A (IV) (*Ac*, m.p. 141·9—142·5°, and *Bz* derivative, m.p. 159·2—159·8°). Nitration of (IV) gives (III). *s*-$C_6H_3Pr^{\beta}_3$ gives the 2-NO_2-derivative, m.p. 74·6—75·5°, which with 96% HNO_3 in H_2SO_4 at 35—53° and finally 100° gives the 2 : 4 : 6-$(NO_2)_3$-derivative, m.p. 190·8—191·6°. Reduction etc. affords 2-*amino*- [*hydrochloride*; *Ac*, m.p. 177·3—178·1°, and *Bz* derivative, m.p. 286·5—287·2° (uncorr.)], 4-*nitro*-2-*amino*-, m.p. 75·9—76·5° (*Ac* derivative, m.p. 157·1—157·9°), and 2 : 4-*diamino*-1 : 3 : 5-*tri*-*iso*propylbenzene, m.p. 71·9—72·7° ($Ac_{(2)}$ derivative, m.p. >360°). Adding 96% HNO_3 (1·76 mols.) to 1 : 2 : 4 : 5-$C_6H_2Pr^{\beta}_4$ in AcOH–Ac_2O at 30—45° and then keeping at 0° gives 3-*nitro*-1 2 : 4 : 5-*tetra*- (V) (15·1%), m.p. 192·6—193·8°, and 5-*nitro*-1 : 2 : 4-*tri*-*iso*propylbenzene-B (VI), m.p. 40·9—41·9° and -C (? a mixture of -*A* and -*B*). Reduction of the -*B* or -*C* forms (VI etc.) gives (IV). Reduction of (V) gives 3-*amino*-1 : 2 : 4 : 5-*tetra*-*iso*propylbenzene, m.p. 150·5—151·3°, oxidised by $K_2Cr_2O_7$ in H_2SO_4–$COMe_2$–H_2O at 30° to *tetra*-*iso*propyl-p-*benzoquinone* (92·3%), m.p. 159·5—160·4°. Physical data are recorded for the oily products. M.p. are corr. except where stated. R. S. C.

New method of nuclear methylation of aromatic amines. (Miss) M. G. Barclay, A. Burawoy, and G. H. Thomson (*J.C.S.*, 1944, 109—112).—Dry distillation (temp. >300°) of anhydro-*p*-aminobenzyl alcohol gives a 1 : 1 mixture (<25%) of NH_2Ph and *p*-toluidine (I), small amounts of *p*-$C_6H_4Me\cdot NHMe$, amines of higher b.p., and NH_3, and much resin. In presence of alkali [*e.g.*, Na_2CO_3; $Ca(OH)_2$] 35—40% of (I) and negligible amounts of by-products are obtained. Anhydro-4-amino-3-methylbenzyl alcohol (from *o*-$C_6H_4Me\cdot NH_2$,HCl and aq. CH_2O) in presence of $Ca(OH)_2$ affords *m*-4-xylidine and some (4 : 3 : 1-$NH_2\cdot C_6H_2Me)_2CH_2$. Anhydro-4-amino-2 : 3-dimethylbenzyl alcohol (from *o*-3-xylidine) gives 4-*amino*-1 : 2 : 3-*trimethylbenzene*, b.p. 238—240°, m.p. 24° (*Ac* derivative, m.p. 140°). Anhydro-4-amino-2 : 5-dimethylbenzyl alcohol (from *p*-xylidine) affords *ψ*-cumidine and some (4 : 2 : 5 : 1-$NH_2\cdot C_6H_2Me_2)_2CH_2$, whilst anhydro-4-amino-3-methoxybenzyl alcohol (from *o*-anisidine) gives a moderate yield of 4 : 1 : 3-$NH_2\cdot C_6H_3Me\cdot OMe$; anhydro-4-amino-1-hydroxymethylnaphthalene (from α-$C_{10}H_7\cdot NH_2$) affords α-$C_{10}H_7\cdot NH_2$ and 4 : 1-$C_{10}H_6Me\cdot NH_2$. (*p*-$NH_2\cdot C_6H_4)_2CH_2$ at 400°/18 hr. yields NH_2Ph and (I). It is suggested that the first-formed radicals $\cdot NH\cdot[C_6H_4\cdot CH_2\cdot NH]_n\cdot C_6H_4\cdot CH_2\cdot$ undergo disproportionation to, *e.g.*, $NH_2\cdot[C_6H_4\cdot CH_2\cdot NH]_n\cdot C_6H_4Me$ or (I) + $\cdot NH\cdot[C_6H_4\cdot CH_2\cdot NH]_{n-1}\cdot C_6H_4\cdot CH_2\cdot$. The reaction can be extended to anhydro-4-aminoaryl alcohols derived from, *e.g.*, NHPhMe. D. G.

Synthesis of *p*-chloroacetanilide. L. Blas and L. Arimany (*Anal. Fis. Quím.*, 1942, **38**, 71—82).—NHPhAc in $(CHCl_2)_2$ at 100—115° with a slow stream of Cl_2, and at 140—150° with a rapid stream of Cl_2, yields exclusively *p*-$C_6H_4Cl\cdot NHAc$ and 2 : 4 : 1-$C_6H_3Cl_2\cdot NHAc$ respectively. F. R. G.

Derivatives of chloral with aromatic amines. W. T. Sumerford and D. N. Dalton (*J. Org. Chem.*, 1944, **9**, 81—84).—Additive [$CCl_3\cdot CH(OH)\cdot NHAr$ (I)] or condensation [$CCl_3\cdot CH(NHAr)_2$ (II)] compounds are obtained by shaking a solution of the amine or its salts in AcOH with $CCl_3\cdot CH(OH)_2$ dissolved in H_2O containing NaOAc at room temp. Thus are obtained *ββδ-trichloro-αα-diarylaminoethanes* in which Ar = o-$C_6H_4\cdot COEt$, m.p. 160°, p-$C_6H_4\cdot CO_2Et$, m.p. 91·5°, p-$C_6H_4\cdot CO_2Me$, m.p. 104°, β-$C_{10}H_7$, m.p. 116—118° m-*tolyl*, m.p. 103·5°, o-C_6H_4Cl, m.p. 104°, p-$C_6H_4\cdot OEt$, m.p. 91°, and *Bz*, m.p. 116°, and *βββ-trichloro-α-arylaminoethanols* in which Ar = o-$C_6H_4\cdot CO_2Me$, m.p. 105°, 2 : 4-$OH\cdot C_6H_3\cdot CO_2Me$, m.p. 93°, and p-$C_6H_4\cdot COMe$, m.p. 93°. When heated at 75° 2 mols. of (I) lose 1 mol. of $CCl_3\cdot CH(OH)_2$ and yield (II). In no instance was it possible to cause (I) to lose the elements of H_2O with production of the Schiff's base. M.p. are corr. H. W.

Relations between chemical activity and absorption in the ultra-violet of organic molecules. VI. Action of nitrosyl chloride on substituted amides of acetoacetic acid. K. G. Naik, R. K. Trivedi, and B. N. Mankad (*J. Indian Chem. Soc.*, 1943, **20**, 384—388).—$CH_2Ac\cdot CO\cdot NHPh$ (in anhyd. C_6H_6) saturated with gaseous NOCl at ~0° and then heated at 100° (bath) gives $NHPh\cdot CO\cdot CAc{:}N\cdot OH$. Similarly the following are obtained: *oximinoacetoacet*-o-, m.p. 130°, and -p-*toluidide*, m.p. 92°, -m-4-*xylidide*, m.p. 145°, -α-, m.p. 138°, and -β-*naphthalide*, m.p. 152°. Contrary to expectation no structural or stereo-isomerides can be isolated. $CH_2Ac\cdot CO\cdot NHAr$ with SO_2Cl_2 in Et_2O gives chloroacetoacet-anilide, m.p. 138°, -m-4-*xylidide*, m.p. 114°, and -α-*naphthalide*, m.p. 135°. (Cf. A., 1944, I, 116.) H. M. C.

Activity of halogen derivatives of substituted amides of malonic acid. I. Action of Grignard's reagent on the chloro-derivatives of substituted amides of malonic acid. II. Velocity of replacement of chlorine atom of the group ·CHCl· in monochloro-derivatives of substituted amides of malonic acid. K. G. Naik, R. K. Trivedi, and S. M. Mehta (*J. Indian Chem. Soc.*, 1943, **20**, 345—348, 355—357).—I. Grignard's reagents (MgPhBr and $CH_2Ph\cdot MgCl$) with $CCl_2(CO\cdot NHAr)_2$ give $CHCl(CO\cdot NHAr)_2$ and no di*tert.*-alcohol. A reaction mechanism is suggested. The second Cl cannot be removed in this way. *Chloromalondi-anilide*, m.p. 176°, -p-, m.p. 212°, and -o-*toluidide*, m.p. 179°, and -m-4-*xylidide*, m.p. 202°, are described.

II. The Cl of $CHCl(CO\cdot NHAr)_2$ (Ar = Ph, *o*- and *p*-tolyl, *m*-4-xylyl) is replaced by H on treatment with HI. The velocity of replacement is influenced by the position of the substituents in the C_6H_3 rings and the mol. wts. of the residues attached to the CO-groups. D. G.

Preparation and properties of *N*-substituted sulphamic acids. L. F. Audrieth and M. Sveda (*J. Org. Chem.*, 1944, **9**, 89—101).—$NHR\cdot SO_3H$ and $NRR'\cdot SO_3H$ are obtained (*a*) by the gradual addition of $ClSO_3H$ to 3 equivs. of the amine in dry $CHCl_3$ at ≯0°: $3NHRR' + ClSO_3H \rightarrow NRR'\cdot SO_3H,NHRR' + NHRR',HCl$, (*b*) by reduction of the NO_2-compound by $Na_2S_2O_4$ in presence of Na_3PO_4 (to prevent the solution from becoming acid): $ArNO_2 + Na_2S_2O_4 + H_2O \rightarrow NHAr\cdot OH + SO_2 + Na_2SO_4$; $NHAr\cdot OH + SO_2 + Na^+ \rightarrow NHAr\cdot SO_3Na + H^+$; the method suffers from the disadvantage of involving large quantities of H_2O-sol. salts which render difficult the isolation of the sulphamates: (*c*) by treatment of the C_5H_5N,SO_3 additive compound (I) with ~2·5 mols. of the requisite amine in a 3-fold vol. of H_2O at 0° followed by addition of a slight excess of the requisite metallic hydroxide; a disadvantage is the relative instability of (I): (*d*) by interaction of amine and $ClSO_3Na$ which occurs thus: $2NH_2R + ClSO_3Na \rightarrow NHR\cdot SO_3H,NH_2R + NaCl$; the addition of NaOH is therefore not avoided and the method has the further disadvantage that technical $ClSO_3Na$ contains 30% of NaCl. The following are described: *Na phenyl-*, *Na* p-*phenetyl-*, *Na* p-*tolyl-*, *Na* N-*phenyl*-N-*methyl-*, *Na benzyl-*, *Na* β-*phenylethyl-*, *Na* γ-*phenylpropyl-*, *Na* n-*hexyl-*, cyclo*hexylammonium*, *Na*, *Ba*, NH_4, m.p. >220°, softens at ~208°, and *Ag* cyclo*hexyl-*, *Na di*cyclo*hexyl-*, *Na* N-cyclo*hexyl*-N-*ethyl-*, *Na* N-cyclo*hexyl*-N-*methyl-*, *Na* 2-*methyl*-cyclo*hexyl-*, and *Na* 1 : 2 : 3 : 4-*tetrahydronaphthyl-sulphamates*. cyclo*Hexyl-*, m.p. 169—170°, and *di*cyclo*hexyl-*, m.p. 161°, *-sulphamic acid* have been prepared. The antipyretic action of these compounds is discussed. The extraordinary sweetness of certain *N*-substituted sulphamic acids is thus far limited to those containing as a substituent (*a*) a *cyclo*hexyl ring which may or may not be substituted and (*b*) a free H on the N, viz., $NHR\cdot SO_2X$, where X is almost any salt-forming group. H. W.

Sulphanilamide derivatives.—See B., 1944, III, 73.

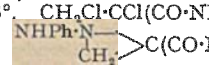
Sulphamlylalkylguanidines.—See B., 1944, III, 73.

***p*-Aminoarylsulphonamidoaryl-*o*-sulphonic acids and their salts.**—See B., 1944, III, 73.

Carbon rings. XXXIV. *cyclo*Decane and its derivatives and the two 9 : 10-diaminodecahydronaphthalenes. P. A. Plattner and J. Hulstkamp (*Helv. Chim. Acta*, 1944, **27**, 220—230).—Largely a repetition and extension of the work of Hückel *et al.* (A., 1930, 76; 1933, 494). Reduction of *cyclo*decane-1 : 6-dionedioxime (corresponding *monoxime*, m.p. 155°) gives varying amount of mono- and di-amines and neutral products. Treatment with Na and EtOH gives ~60% of basic components relatively poor in *cyclo*decane derivatives. Replacement of EtOH by amyl alcohol gives nearly 100% of bases, essentially a mixture of α- (I) and β- (II) -1 : 6-diamino*cyclo*decane with cis- (III) and trans- (IV) -9 : 10-*diamino-decahydronaphthalene*. The reaction product is distilled and dissolved in EtOH which is saturated with CO_2, causing the pptn. of the sparingly sol. carbamates of (I) and (II). The bases regenerated therefrom are purified through their hydrochlorides. Thus are obtained (I), b.p. 145°/12 mm., m.p. 43—46° (yield 40%), probably the *trans*-compound and identical with Hückel's base, m.p. 50° (Ac_2 derivative, m.p. 296°; *dipicrate*, decomp. 280—285°; *dihydrochloride*, slow decomp. >200°), and (II) (yield 20%), b.p. 145°/12 mm., m.p. 8—10° [*dihydrochloride* (+$2H_2O$), gradual decomp. >200°; Ac_2 derivative, m.p. 253°; mono-, decomp. 200—210°, and *di-picrate*, decomp. 247—252°]. The portion of the basic mixture which gives EtOH-sol. carbamates or does not give a carbamate consists mainly of (III), b.p. 121°/12 mm., m.p. 41° [*dihydrate*; *dihydrochloride* (+$1H_2O$); Ac_2 derivative, m.p. 242°; *mono-*, m.p. 236° (decomp.), and *di-picrate*, decomp. 242—247°]. (IV) is present to the extent of ~3% and is identified by comparison with the product of the reduction of *trans*-9 : 10-dinitrodecahydronaphthalene; it has m.p. 70°, b.p. ~120°/12 mm., and gives a *di-picrate*, decomp. 262—264°, and an Ac_2 derivative, m.p. >360°.

The constitution of (**III**) and (**IV**) is established by conversion by HNO_2 into 2-*spirocyclo*pentano*cyclo*hexanone. The basic mixture appears to contain further cryst. compounds partly of hydroazulene structure. (**I**) is transformed by MeI and 5N-KOH–MeOH into *α-di*-1 : 6-*dimethylamino*cyclo*decane dimethiodide*, decomp. 305—320°, converted by Ag_2O into the quaternary base, which when decomposed thermally yields cyclo*decadiene*, b.p. 69°/12 mm., hydrogenated (Adams) to *cyclo*decane (**V**), b.p. 75°/12 mm., m.p. 9·5°. Analogously (**II**) affords *β-di*-1 : 6-*dimethylamino*cyclo*decane dimethiodide*, decomp. 310—330°, which is converted into (**V**), m.p. 9·4°. (**II**) is transformed by MeI and KOH–MeOH into bisdimethylaminodecahydronaphthalene dihydriodide (corresponding *base*, m.p. 86°). H. W.

1 : 4-Diamino-2-methylnaphthalene.—See B., 1944, II, 129.

Relations between chemical activity and absorption in the ultra-violet of organic molecules. IV. Interaction of phenylhydrazine with the chloro-derivatives of substituted amides of malonic acid. K. G. Naik, R. K. Trivedi, and C. M. Mehta (*J. Indian Chem. Soc.*, 1943, **20**, 369—371; cf. A., 1944, I, 116).—$CCl_2(CO{\cdot}NHAr)_2$ with $NHPh{\cdot}NH_2$ (**I**) in boiling EtOH gives $NHPh{\cdot}N{:}C(CO{\cdot}NHAr)_2$; in the cold $NHPh{\cdot}NH{\cdot}CCl(CO{\cdot}NHAr)_2$ results. The following are described: *mesoxal-dianilide-*, m.p. 175°, *-di*-m-*chlorotoluidide-*, m.p. 196°, *-di*-p-, m.p. 185°, and *-di*-o-*toluidide-*, m.p. 148°, *-di*-m-4-*xylidide-*, m.p. 172°, *-mono*-p-*toluidide-*, m.p. 195°, and *-mono-chloroanilide-phenylhydrazone*, m.p. 189—190°; *α-chloro-α-phenylhydrazinomalondi-anilide*, m.p. 179°, -p-, m.p. 210—211°, and -o-*toluidide*, m.p. 158°, -m-*chlorotoluidide*, m.p. 218—219°, and -m-4-*xylidide*, m.p. 206°. $CH_2Cl{\cdot}CCl(CO{\cdot}NH{\cdot}C_6H_4Me)_2$ and (**I**) give almost quant. yields of  ; 1-*anilino*-2 : 2-*di*-o-, m.p. 145°, and -p-*tolylcarbamylaziridine*, m.p. 190°, are described. H. M. C.

Action of cuprous oxide on diazotised amines. III. Action in sulphuric acid–glacial acetic acid. H. H. Hodgson, S. Birtwell, and E. Marsden (*J.C.S.*, 1944, 112—113; cf. A., 1943, II, 158).—Deamination by Cu_2O in H_2SO_4–AcOH attains >70% efficiency for amines of the $C_{10}H_8$ series, but is <40% for those of the C_6H_6 series. Efficiency ∝ the positivity of the C atom to which the diazo-group is attached. D. G.

Manufacture of phenols.—See B., 1944, II, 129.

Hydrogen bonding. Nitrocresols. Nitrodihydroxybenzenes.—See A., 1944, I, 129.

Iodination of 4-hydroxydiphenyl. J. C. Colbert, H. W. Houghton, H. R. Schmidt, and J. L. Abernethy (*J. Amer. Chem. Soc.*, 1944, **66**, 122—124).—With 1 mol. of I in KI, *p*-$C_6H_4Ph{\cdot}OH$ (**I**) in aq. NH_3 (91·1% yield) or, less well, in NaOH or with ICl in AcOH gives 3-*iodo*-4-*hydroxydiphenyl*, m.p. 115—116°, which in C_5H_5N yields a *benzoate*, m.p. 99·5—100°, and with conc. HNO_3 in AcOH gives a (?5-)NO_2-derivative, m.p. 95—100° (decomp.). Attempts to di-iodinate (**I**) in NaOH by I–KI give a *compound*, $C_{24}H_{16}O_2I_2$, m.p. 170—171° (decomp.), but I–KI in aq. NH_3 or ICl–AcOH yields 3 : 5-*di-iodo*-4-*hydroxydiphenyl*, m.p. 95—97° (86—87°) (*benzoate*, m.p. 159—160°). Tri-iodination could not be achieved. R. S. C.

Phosphoric acid esters of phenols. F. L. Breusch and H. Keskin (*Rev. Fac. Sci. Istanbul*, 1942, **7**, 182—189).—$POCl_3$ and the corresponding phenol gave on warming *tri*-m-*tolyl* (**I**), b.p. 258—263°/4 mm., m.p. 25—26°, *tri*-p-*xylyl*, m.p. 77°, *tri*-2 : 4 : 6-*trichlorophenyl*, m.p. 200—201°, and *di*-o-*chlorophenyl phosphate*, m.p. 121·5° (separated from the tri-ester by solubility of the latter in PhMe). Br and (**I**) give *tri*-6-*bromo*-m-*tolyl phosphate*, m.p. 90°. Br and $(p\text{-}C_6H_4Me)_3PO_4$ give *tri*-3 : 5-*dibromo*-p-*tolyl phosphate*, m.p. 178°, hydrolysed to 2 : 6 : 4 : 1-$C_6H_2Br_2Me{\cdot}OH$. Triaryl phosphates are hydrolysed by alkali (curves given) but are stable towards acid reagents. Solubility data are also given. D. G.

Anomalous oxidation of an ethylene derivative by perbenzoic acid. C. K. Bradsher (*J. Amer. Chem. Soc.*, 1944, **66**, 45—46).—*o*-$C_6H_4Ph{\cdot}MgI$ (**I**) with an excess of PhCHO in boiling C_6H_6 gives *o*-$C_6H_4Ph{\cdot}COPh$ (69·5%), m.p. 86—87°, which with MgMeI and then $KHSO_4$ gives *o*-$C_6H_4Ph{\cdot}CPh{:}CH_2$ (**II**) (56—73%), m.p. 59—61°, b.p. 201—202·5°/12 mm., obtained much less well from (**I**) and COPhMe. With BzO_2H in Et_2O at room temp., (**II**) gives a "*di-oxide*," $C_{20}H_{16}O_2$ (46%), m.p. 111—112°, converted by boiling 34% aq. HBr–AcOH, $KHSO_4$ at 170—180°, or conc. H_2SO_4 at 100° (2 min.) into 10-phenyl-9-phenanthrol. R. S. C.

Diphenylyl β-methylallyl ethers.—See B., 1944, II, 129.

α-Bromo-αββ-tri-*p*-anisylethylene.—See B., 1944, II, 130.

Derivatives of 4 : 4′-diaminodiphenyl sulphone.—See B., 1944, III, 74.

Synthesis and chemical properties of diasone [disodium formaldehydesulphoxylate-diaminodiphenyl sulphone].—See A., 1944, III,

Preparation of *cyclo*hexanols by catalytic reduction of phenols. H. E. Ungnade and A. D. McLaren (*J. Amer. Chem. Soc.*, 1944, **66**, 118—122).—In presence of Raney Ni at, usually, 100—300 atm. phenols are reduced in excellent yield to *cyclo*hexanols, substitution having little effect unless two *o*-substituents are present; 2 : 6 : 1-$C_6H_3Pr^{\alpha}_2{\cdot}OH$ (**I**) is unaffected at 360°, but 4 : 2 : 6 : 1-$C_6H_2MeEt_2{\cdot}OH$ (**II**) gives 1-*methyl*-3 : 5-*diethylcyclohexane*, b.p. 175—176·5°. Presence of a small amount of 40% NaOH slightly lowers the temp. required for reduction (normally 125—200°) and permits reduction of (**I**) to *cis-cis*-2 : 6-di-*n*-propyl*cyclo*hexanol, m.p. 109—110°, b.p. 241—242° (phenyl-, m.p. 145·5—146·5°, and *α-naphthyl-urethane*, m.p. 137—138°) (cf. Vavon *et al.*, A., 1937, II, 287), and of (**II**) to mixed 4-methyl-2 : 6-diethyl*cyclo*hexanols [90% including a *form*, m.p. 86—87°, b.p. 219—220° (*α-naphthylurethane*, m.p. 143·5—144°)]. In general only one stereoisomeride is formed, but 4 : 2 : 1-$C_6H_3MeBu^{\gamma}{\cdot}OH$ gives only 4-*methyl*-2-tert.-*butyl*cyclo*hexanol* (91%), b.p. 215—216° (*α-naphthylurethane*, m.p. 130—131°), in absence of NaOH (at 160—190°) but in its presence (at 195—220°) yields also 27% of a *form*, m.p. 112—113° (*α-naphthylurethane*, m.p. 130·5—131·5°) (both forms yield the same *cyclo*hexanone). At 110—125°/1200 lb. *p*-$C_6H_4Ph{\cdot}OH$ gives 4-*cyclo*hexyl*cyclo*hexanol (59·2%), *p-cyclo*hexylphenol (25·7%), and 4-phenyl*cyclo*hexanol (7·4%), but in presence of NaOH at 95—115° gives more rapidly 43·2, 16·6, and 30·3%, respectively. Hydrogenation of *o*-allyl-, *o*-propenyl-, or 2 : 6-diallyl-phenol gives the alkylphenol very rapidly at 50° and then the alkyl*cyclo*hexanol at 140—160°; alkali catalyses both reactions. Acylphenols in EtOH at ~110° give good yields of alkylphenols and then at 180° (usually *cis-*)alkyl*cyclo*hexanols, isolation of the alkylphenol being unnecessary; in presence of alkali at 45—65° mixtures of alkylphenols and hydroxyalkyl*cyclo*hexanols are obtained; at 110° mixtures of alkyl- and hydroxyalkyl-*cyclo*hexanols are formed; some hydrogenolysis of the OH of the hydroxyalkyl*cyclo*hexanols occurs during this second stage, but it cannot be completed even at 220° and is thus probably catalysed by the Na phenoxide. Incidentally are described *trans*-4-methyl-, b.p. 167—170° (3 : 5-dinitrobenzoate, m.p. 137·2—138·7°; phenyl-, m.p. 124—124·5°, and *α-naphthyl-urethane*, m.p. 156·5—157·5°), *cis*-2-ethyl-, b.p. 180—182° (phenyl-, m.p. 99—99·8°, and *α-naphthyl-urethane*, m.p. 151—153·5°), 3-*ethyl*-, b.p. 191·5—192° (*α-naphthyl-urethane*, m.p. 98·5—99·5°), 4-ethyl-, b.p. 191—192° (phenyl-, m.p. 114—115°, and *α-naphthyl-urethane*, m.p. 139·5—140·5°), *cis*-2-*n*-propyl-, b.p. 201·5—202° (phenyl-, m.p. 94—95°, and *α-naphthyl-urethane*, m.p. 103—104°), (?*cis-trans-*)2 : 4-, b.p. 176·5—177·5° (phenyl-, m.p. 95—96°, and *α-naphthyl-urethane*, m.p. 152·5—153·5°), *cis-trans*-2 : 5-, b.p. 179—180·5° (phenyl-, m.p. 116—117°, and *α-naphthyl-urethane*, m.p. 172—173·5°), 3 : 4-, b.p. 188—189·5° (phenyl-, m.p. 96—97°, and *α-naphthyl-urethane*, m.p. 162—163°), and *cis-cis*-3 : 5-dimethyl-, m.p. 8—9·8°, b.p. 181—183° (phenyl-, m.p. 106—107·5°, and *α-naphthyl-urethane*, m.p. 141—143°), 2 : 3 : 5-, b.p. 196—197° (*α-naphthylurethane*, m.p. 148—149°), and 2 : 4 : 6-*trimethyl*-, m.p. 70·5—71°, b.p. 182—184° (*α-naphthylurethane*, m.p. 197·5—198°), 4-*α-hydroxyethyl*-, m.p. 91—92·2° (*di*-3 : 5-*dinitrobenzoate*, m.p. 210—212°), and 2-*α-hydroxy*-n-*propyl*-, b.p. 256—259° (*di*-3 : 5-*dinitrobenzoate*, m.p. 162·5—164°), -cyclo*hexanol*.

4 : 4′-Dihydroxy-3 : 3 : 5′ : 5′-tetra(hydroxymethyl)diphenylmethane. F. Seebach (*Ber.*, 1940, **73**, [*B*], 1338—1346).—The compound regarded previously as 1 : 2 : 6-$OH{\cdot}C_6H_3(CH_2{\cdot}OH)_2$ (A., 1939, II, 476) is shown to be 4 : 4′-*dihydroxy*-3 : 5 : 3′ : 5′-*tetra*(*hydroxymethyl*)-*diphenylmethane* (**I**). The Mg, *Cu*, Li_2, Na_2, *Ca*, and (*FeOH*) compounds are described. The triacetate (*loc. cit.*) is the *hexa-acetate* of (**I**). (**I**) is converted by CH_2N_2 (not Me_2SO_4 or MeI) into 4 : 4′-*dimethoxy*-3 : 3′ : 5 : 5′-*tetra*(*hydroxymethyl*)*diphenylmethane*, m.p. 115°, oxidised by $KMnO_4$ at 95° to 4 : 4′-*dimethoxybenzophenone*-3 : 5 : 3′ : 5′-*tetracarboxylic acid* (+AcOH) (**II**), m.p. 216° (*oxime*, m.p. 265°; Me_4 ester, m.p. 158°), hydrolysed by HI to 4 : 4′-*dihydroxybenzophenone*-3 : 5 : 3′ : 5′-*tetracarboxylic acid*, m.p. 310° (*Mg H* salt). This is transformed by KOH at 310° into 4 : 1 : 3 : 5-$OH{\cdot}C_6H_2(CO_2H)_3$, m.p. 306°, and 2 : 1 : 3-$OH{\cdot}C_6H_3(CO_2H)_2$, m.p. 241°. (**II**) is decarboxylated in boiling quinoline to $CO(C_6H_4{\cdot}OH\text{-}p)_2$, m.p. 206°, methylated to $CO(C_6H_4{\cdot}OMe\text{-}p)_2$, m.p. 141°. H. W.

4-Phenyl-2-methyl*cyclo*hexylacetic acid and related compounds. C. K. Chuang, J. H. Chu, and Y. S. Kao (*Ber.*, 1940, **73**, [*B*], 1347—1353).—Et 1-hydroxy-2-methyl*cyclo*hexylacetate is converted by $SOCl_2$ and C_5H_5N into a mixture of Et 2-methyl-Δ^1-*cyclo*hexenylacetate and Et 2-methyl*cyclo*hexylideneacetate, transformed by C_6H_6 and $AlCl_3$ (2 mols.) at room temp. into a *product*, b.p. 165—167°/2 mm. (saturated towards Br in CCl_4 and alkaline $KMnO_4$), hydrolysed by alkali to a mixture (**I**) from which 4-phenyl-2-methyl-*cyclo*hexylacetic acid (**II**), m.p. 126—128° (*amide*, m.p. 183—184°), is isolated. 2-Phenyl-2-methyl*cyclo*hexylacetic acid cannot be present in (**I**), which is not cyclised to the corresponding hexahydrophenanthrone by 85% H_2SO_4 or anhyd. $ZnCl_2$. (**II**) is esterified ($EtOH–H_2SO_4$), dehydrogenated (S at 220—230°), and hydrolysed (KOH–EtOH) to 3-*methyldiphenyl*-4-*acetic acid*, m.p. 145°. Et 4-phenyl-2-methyl*cyclo*hexylacetate and MgPhBr give the non-cryst. diphenylcarbinol, which is oxidised by CrO_3 in AcOH to 4-*phenyl*-2-*methyl*cyclo*hexanecarboxylic acid*, m.p. 140—141° (amide, m.p.

176—177°), dehydrogenated and decarboxylated by Se at 330—340° to 3-methyldiphenyl, identified by oxidation to diphenyl-3-carboxylic acid, m.p. 165—166°. Me 4-phenyl-2-methyl*cyclo*hexanecarboxylate is dehydrogenated by S at 220—240° and then hydrolysed to 3-methyldiphenyl-4-carboxylic acid (Me ester, m.p. 62—63°). H. W.

Synthesis of coumarins from *o*-hydroxyaryl alkyl ketones. IV. Formation of *o*-coumaric acids from *o*-hydroxyaldehydes. D. Chakravarti and S. A. Momen (*J. Indian Chem. Soc.*, 1943, **20**, 338—340).—2 : 5 : 1-OMe·C_6H_3Me·CHO, 2 : 4 : 1-$(OMe)_2C_6H_3$·CHO, and 2 : 1-OMe·$C_{10}H_6$·CHO condensed with $CH_2Br·CO_2Et$ and CHMeBr·CO_2Et gave OH-esters, which on dehydration and hydrolysis gave *trans-o*-coumaric acids. *o*-OMe-aldehydes always give *trans-o*-methoxycinnamic acids by Perkin's, Chakravarti and Majumdar's, and $CH_2(CO_2H)_2$ condensations. The following appear new: trans-2-*methoxy*-5-*methyl*-, m.p. 145—146° (*Et* ester, b.p. 165°/7 mm.), trans-2-*methoxy*-α : 5-*dimethyl*-, m.p. 109—110° (*Et* ester, b.p. 160°/5 mm.), and trans-2 : 4-*dimethoxy*-α-*methyl*-*cinnamic acid*, m.p. 130° (*Et* ester, b.p. 200°/6 mm.); β-2-*methoxy*-1-*naphthyl*-, m.p. 153—154° (*Et* ester, b.p. 210—212°/4 mm.), and β-2-*methoxy*-1-*naphthyl*-α-*methyl*-*acrylic acid*, m.p. 138—139° (*Et* ester, b.p. 220—225°/5 mm.). Et β-hydroxy-β-4-methoxy-*m*-tolylpropionate has b.p. 200°/12 mm. D. G.

Transamination reaction. Effect of various nuclear substituted α-amino-α-phenylacetic acids on the course of the reaction. E. K. Harvill and R. M. Herbst (*J. Org. Chem.*, 1944, **9**, 21—30).—The reaction between $AcCO_2H$ and various NH_2-acids is followed by the determination of CO_2 evolved after definite intervals of time and the characterisation of volatile and non-volatile aldehydes produced. In the reaction between $AcCO_2H$ and *p*-OH·C_6H_4·$CH(NH_2)·CO_2H$, new m.p. 240—241° (decomp.), sublimes at 229°, *p*-OMe·C_6H_4·$CH(NH_2)·CO_2H$, decomp. 248—285°, sublimes at 230°, and α-*amino*-α-*o*-*anisylacetic acid* (+H_2O), m.p. 161—162° [*Cu* salt (+$2H_2O$)], both MeCHO and an aromatic aldehyde are formed with alanine (**I**) and CO_2 whereas in the change between $AcCO_2H$ and α-*amino*-α-*p*-*chlorophenyl*-, m.p. 261—262° (decomp.), -*o*-*chlorophenyl*-, m.p. 219·5°, and -*o*-*hydroxyphenyl*-, m.p. 194—195° (decomp.), -*acetic acid* only an aromatic aldehyde is produced with (**I**) and CO_2. In the system, $CO_2H·CH(C_6H_4Y)·N:CMe·CO_2H \rightarrow C_6H_4Y·CH:N·CHMe·CO_2H + CO_2$, the rate of formation of CO_2 increases with increasing dipole moment of C_6H_4Y. The effect of the same group is enhanced by shifting it from the *p*- to the *o*-position. In their effect on the rate of formation of CO_2 the groups studied fall into the order: *o*-Cl > *o*-OMe > *o*-OH > *p*-Cl > *p*-OMe > *p*-OH. α-*Amino*-α-2-*furylacetic acid* has m.p. 212—213° (decomp.). The NH_2-acids are obtained by hydrolysis with $Ba(OH)_2$ of the 5-*arylhydantoins*, CHR·NH / CO—NH >CO, prepared from the appropriate aldehyde, KCN, and $(NH_4)_2CO_3$ in aq. EtOH. Compounds are described in which R = *p*-anisyl, m.p. 195° (lit. 191·5°), *o*-anisyl (**II**), m.p. 189° (lit. 186—187°), p-C_6H_4Cl·, m.p. 191°, *o*-C_6H_4Cl·, m.p. 175—176°, *p*-OH·C_6H_4·, m.p. 269—270° (decomp.) [lit. 263° (decomp.)], *o*-*OH*·C_6H_4· (**III**), m.p. 240—244° (decomp.), and *furyl*, two forms, m.p. 101° and 147°. (**III**) could not be obtained by the general procedure but results from the hydrolysis of (**II**) by HI (*d* 1·5). The NH_2-acids and PhNCO in alkaline solution give α-*phenylcarbamido*-α-*arylacetic acids*, in which Ar = p-*anisyl*, m.p. 196° (decomp.), o-*anisyl*, m.p. 186·2°, p-C_6H_4Cl·, m.p. 185·5°, o-C_6H_4Cl·, m.p. 177—179°, *p*-OH·C_6H_4·, m.p. 192° (decomp.), and 2-furyl, m.p. 147° (decomp.). These are converted by boiling HCl into 3-*phenyl*-5-*arylhydantoins*, CHR·NH / CO—NPh >CO, in which R = p-*anisyl*, m.p. 179°, o-*anisyl*, m.p. 134°, *p*-C_6H_4Cl·, m.p. 167—168° o-C_6H_4Cl·, m.p. 187·5°, p-*OH*·C_6H_4·, m.p. 171° and 201° after resolidification, and o-*OH*·C_6H_4·, m.p. 224—225°. M.p. are corr. H. W.

Dialkyl phenyl- and phenylalkyl-malonates.—See B., 1944, II, 130.

9 : 9-Di-β-carbamylethylfluorene.—See B., 1944, II, 129.

[Attempted] synthesis of caryophyllenic acid. M. D. Owen (*J. Indian Chem. Soc.*, 1943, **20**, 343—344).—The condensation product of CMe_2:CO and *cyclo*pentadiene was oxidised ($COMe_2$–$KMnO_4$ at 4°) to 4-*keto*-2-*carboxy*-3 : 3-*dimethyl*cyclo*butylacetic acid* (?) (**I**), m.p. 124—125°. Attempts to reduce (**I**) to caryophyllenic acid have so far been unsuccessful. D. G.

Amidine salts.—See B., 1944, II, 129.

Lignin. XLII. Vanillincarboxylic acid and related acids. K. Freudenberg and F. Klink (*Ber.*, 1940, **73**, [*B*], 1369—1376).—Me 2-hydroxy-3-methoxy-5-allylbenzoate is not isomerised by KOH in boiling C_5H_{11}·OH or by KOH–MeOH at 135° but is converted by at 220—235° into 2-*hydroxy*-3-*methoxy*-5-*propenylbenzoic acid* (**I**), m.p. 157° (*Me* ester, m.p. 73·5°; *acetate*, m.p. 141°), which when ozonised in EtOAc and then hydrogenated (Pd–C in EtOAc) affords 2-hydroxy-5-aldehydo-3-methoxybenzoic (vanillin-5-carboxylic) acid, m.p. 255° (decomp.). (**I**) is converted by Me_2SO_4 and NaOH at room temp. into 2 : 3-*dimethoxy*-5-*propenylbenzoic acid*, m.p. 101°, ozonised and hydrogenated to 5-*aldehydo*-2 : 3-*dimethoxybenzoic acid*, m.p. 152°, and oxidised by $KMnO_4$–$NaHCO_3$ to *iso*hemipinic acid (**II**), m.p. 255°. (**I**) is treated with $PhSO_2Cl$ in C_5H_5N and then oxidised ($KMnO_4$–$NaHCO_3$) and hydrolysed (NaOH) to 4-*hydroxy*-5-*methoxyisophthalic acid*, m.p. 276°. 4 : 5 : 1 : 3-OH·C_6H_2(OMe)$(CHO)_2$ is methylated to 4 : 5 : 1 : 3-$(OMe)_2C_6H_2(CHO)_2$, m.p. 125°, oxidised to (**II**), which is converted by boiling AcOH–48% HBr into 4 : 5 : 1 : 3-$(OH)_2C_6H_2(CO_2H)_2$ (**III**), m.p. 291° [*Me*$_2$ ester, (**IV**), m.p. 139°]. Partial esterification of (**III**) by MeOH–H_2SO_4 gives 1-*Me H* 4 : 5-*dihydroxyisophthalate*, m.p. 216°. (**IV**) is transformed by successive treatment with MeOH–NaOMe and $-CH_2I_2$ at 140° into *Me*$_2$ 4 : 5-*methylenedioxyisophthalate*, m.p. 145—146°, hydrolysed (KOH–MeOH) to the *acid*, m.p. 293—294° (decomp.). Guaiacoldialdehyde is demethylated to 4 : 5-*dihydroxyisophthalaldehyde*, m.p. 200° (*bisphenylhydrazone*, m.p. 249°), which yields 4 : 5-*methylenedioxyisophthalaldehyde*, m.p. 153—154°. H. W.

***o*-Aldehydocarboxylic acids. IV. Synthesis of 5 : 6-methylenedioxyphthalaldehydic acid.** S. N. Chakravarti (*J. Indian Chem. Soc.*, 1943, **30**, 382—383).—5 : 6-Methylenedioxyhomophthalic acid (modified prep.; cf. Haworth *et al.*, A., 1926, 951) was oxidised (SeO_2 in boiling xylene) to 5 : 6-methylenedioxyphthalonic acid, converted through its $NaHSO_3$ compound into 5 : 6-*methylenedioxyphthalaldehydic acid*, m.p. 155°, which was reduced (Na–Hg; dil. NaOH) to 5 : 6-*methylenedioxyphthalide*, m.p. 227°. H. M. C.

Lignin and related compounds. LXXIV. Relation of wood ethanolysis products to the Hibbert series of plant respiratory catalysts. Allylic and dismutation rearrangements of γ-chloro-α-3 : 4-dimethoxyphenylpropan-β-one and α-bromo-3 : 4-dimethoxyphenylpropan-β-one. A. M. Eastham, H. E. Fisher, M. Kulka, and H. Hibbert (*J. Amer. Chem. Soc.*, 1944, **66**, 26—32; cf. A., 1944, II, 115).—The ease with which rearrangements, $CH_2Ar·CO·CH_2X \rightarrow CHArX·COMe \rightarrow COAr·CHMeX$, occur supports Hibbert's view that the C_6—C_3 products isolated after ethanolysis of wood are stabilised end-products formed from progenitors of the coniferyl alcohol type. 3 : 4 : 1-$(OMe)_2C_6H_3·CH:CMe·NO_2$ with $FeCl_3$, Fe dust, and HCl gives the oxime, which by hydrolysis yields *veratryl Me ketone* (**I**) (70%), b.p. 118°/0·2 mm., which with Br and a trace of Bz_2O_2 in $CHCl_3$ gives α-*bromoveratryl Me ketone* (**II**) (58%), m.p. 87—88° (*semicarbazone*, m.p. 201·5—202·5°). With 5% KOAc at 100° (**II**) gives α-*hydroxyveratryl Me ketone* (**III**) (55%), m.p. 76—77° (*semicarbazone*, m.p. 155—156°), which is unchanged by 5% KOAc at 100° (CO_2) and with AcCl–C_5H_5N yields the oily α-*acetate* (89%) (2 : 4-*dinitrophenylhydrazone*, m.p. 149—150°), also obtained from (**I**) by $Pb(OAc)_4$–AcOH at 88°. 3 : 4 : 1-$(OMe)_2C_6H_3·CHCl·CO·NH_2$ and HI in AcOH at room temp. give 3 : 4 : 1-$(OMe)_2C_6H_3·CH_2·CO·NH_2$ and thence, successively, the acid, acid chloride, CHN_2 ketone (**IV**), and *veratryl* CH_2Br *ketone* (80%), m.p. 44—45°. In boiling AcOH, (**IV**) gives *veratryl* CH_2·*OAc ketone* (85%), m.p. 55—56° (*semicarbazone*, m.p. 128—129°). $CuSO_4$ oxidises (**III**) or 3 : 4 : 1-$(OMe)_2C_6H_3Cl·CHMe·OH$ (**V**) (*semicarbazone*, m.p. 154—155°) in aq. C_5H_5N at 100° to α-3 : 4-*dimethylphenylpropane*-αβ-*dione* (**VI**), m.p. 69—70°. With AgOAc in boiling EtOH–CO_2 (**II**) or 3 : 4 : 1-$(OMe)_2C_6H_3·CH_2·CO·CH_2Cl$ (**VII**) gives 3 : 4 : 1-$(OMe)_2C_6H_3·CH(OEt)·COMe$ (**VIII**). 2% HCl–EtOH–CO_2 converts (**III**) into (**VIII**) and 3 : 4 : 1-$(OMe)_2C_6H_3·CO·CHMe·OEt$. With boiling 5% KOAc, (**VII**) gives (**III**) and (**V**) [?(**VI**)], but with KOAc–AcOH at 90—100° gives 3 : 4 : 1-$(OMe)_2C_6H_3·CO·CHMe·OAc$. 5% H_2SO_4 at 70—80° has no effect on (**III**), nor has boiling 5% KOAc on (**V**). NaOMe–MeOH or KOH–MeOH converts (**VII**) at room temp. into (?) α-*methoxy*-α-*veratrylethylene oxide*, m.p. 40—41°; the (?) α-*ethoxy*-analogue, b.p. 104°/0·04 mm., is similarly obtained by NaOEt or KOH–EtOH. R. S. C.

Use of phenyl esters in the Reformatsky reaction. M. S. Bloom and C. R. Hauser (*J. Amer. Chem. Soc.*, 1944, **66**, 152—153).—RCO_2Ph and CR′R″Br·CO_2Et undergo the Reformatsky reaction in boiling PhMe–C_6H_6 satisfactorily if neither component has H on $C_{(\alpha)}$; $CMe_2Br·CO_2Et$ with PhOBz gives 52% of $CMe_2Bz·CO_2Et$, with *p*-$C_6H_4Ph·OAc$ gives 11% of $CMe_2Ac·CO_2Et$, and does not condense with EtOBz; very low yields of β-CO-ester are obtained from $CH_2Br·CO_2Et$ by PhOBz or $EtCO_2·C_6H_4Ph$-*p*. All the Zn is nevertheless used when the reaction fails; probably condensation of the Ph esters (with H at $C_{(\alpha)}$) and enolisation of the β-CO-ester are caused by the Zn alkyl halide. R. S. C.

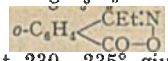
***cyclo*Alkenyl methyl ketones.**—See B., 1944, II, 130.

Absorption spectra and structure of pyrethrins I and II.—See A., 1944, I, 97.

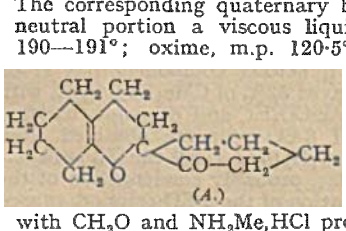
Preparation of *cyclo*pentenones from lactones. R. L. Frank, P. G. Arvan, J. W. Richter, and C. R. Vanneman (*J. Amer. Chem. Soc.*, 1944, **66**, 4—6).—Et lævulate (prep. in 81% yield by distilling a solution of the acid and a little conc. H_2SO_4 in EtOH–C_6H_6), b.p. 93—94°/18 mm., with *n*-C_6H_{13}·MgCl in boiling Et_2O–C_6H_6 gives γ-*methyl*-γ-n-*decolactone* (28%; C_6H_{13}·MgBr gives 31%), b.p. 120—125°/4—5 mm., which with P_2O_5 gives 50% of dihydrojasmone and with Br in CCl_4 at room temp. and then 70—75° (ultra-violet light) gives (?) $C_6H_{13}·CMeBr·CH_2·CHBr·CO_2H$, converted by distillation into α-*bromo*-γ-*methyl*-γ-n-*decolactone*, b.p. 121—122°/1 mm. With NaOMe–MeOH at room temp. this gives α-*methoxy*-γ-*methyl*-γ-n-*decolactone* (65%), b.p. 107—108°/3 mm. (and a *substance*, $C_{11}H_{22}O_3$,

b.p. 151—170°/3—4 mm.), which with P_2O_5 gives a hydrocarbon, b.p. 74—82°/3—5 mm., and (?) *β-methyl-γ-n-nonolactone*, b.p. 112—115°/3—5 mm. R. S. C.

1 : 3-Rearrangement of a phenyl group. C. F. H. Allen and J. Van Allan (*J. Amer. Chem. Soc.*, 1944, **66**, 7—8).—1 : 3-Migration of Ph is proved (cf. A., 1943, II, 325). 2 : *o*-Diphenyl-3 : 4-di-*p*-bromophenyl*cyclo*pentadienone and MgPhBr give 1 : 2 : 5-*triphenyl*-3 : 4-*di*-p-*bromophenyl*-$\Delta^{2:4}$-cyclo*pentadienol* (**I**), m.p. 195°, which gives a red colour in H_2SO_4, shows one active H but does not add MgMeI, and with $(CH{\cdot}CO)_2O$ at 200° gives 3 : 6-*diphenyl*-4 : 5-*di*-p-*bromophenyl*-3 : 6-endo-*α-hydroxybenzylidene*-Δ^4-*tetrahydrophthalic anhydride*, m.p. 222°. At 260—265°/14 mm., (**I**) rearranges to 2 : 3 : 5-*triphenyl*-3 : 4-*di*-p-*bromophenyl*-Δ^4-cyclo*pentenone*, m.p. 178°, which gives a yellow colour in H_2SO_4, adds 1 MgMeI but shows no active H, and with CrO_3–AcOH gives *p*-$C_6H_4Br{\cdot}COPh$ (53·5%) (2 : 4-*dinitrophenylhydrazone*, m.p. 207—209°), BzOH (63%), and *p*-$C_6H_4Br{\cdot}CO_2H$ (32%). R. S. C.

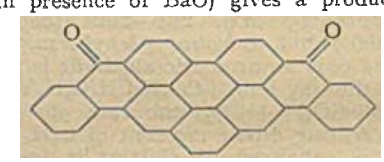
2 : 3-Disubstituted indones. R. L. Frank, H. Eklund, J. W. Richter, C. R. Vanneman, and A. N. Wennerberg (*J. Amer. Chem. Soc.*, 1944, **66**, 1—4).—Adding 2-phenylindane-1 : 3-dione, m.p. 144—145°, in much C_6H_6 or PhMe to 3—4 mols. of MgRHal in C_6H_6 gives 2-*phenyl*-3-*methyl*- (40%), m.p. 67—68° (*phenylhydrazone*, m.p. 120°), -3-*ethyl*- (**I**) (42%), m.p. 97—98° (*phenyl*-, m.p. 96—97°, and 2 : 4-*dinitrophenyl*-*hydrazone*, m.p. 206—207°), and -3-cyclo*hexyl*-*indone* (10%), m.p. 163—164° (*phenylhydrazone*, m.p. 166—167°), and 2 : 3-diphenylindone (48%), m.p. 152—153°. Phthalide, ArCHO, and NaOEt–EtOH give 2-anisyl- (34·6%), m.p. 153—154°, and 2-3′ : 4′-*dimethoxyphenyl*-*indane*-1 : 3-*dione* (33·4%), m.p. 188—190°, and thence, as above, 2-*anisyl*-3-*ethyl*- (42%), m.p. 119—120° (*phenylhydrazone*, m.p. 156—157°), and -3-iso*propyl*- (23%), m.p. 138—139°, b.p. 198—203°/2 mm. (*phenylhydrazone*, m.p. 166—168°), and 2-3′ : 4′-*dimethoxyphenyl*-3-*ethyl*- (27%), m.p. 111—112°, b.p. 192—195°/4 mm. (*phenylhydrazone*, m.p. 188—190°), -*indone*. $CHEtBr{\cdot}CO_2Et$, $COPh_2$, and Zn in C_6H_6 give $OH{\cdot}CPh_2{\cdot}CHEt{\cdot}CO_2Et$, cyclised by conc. H_2SO_4 at room temp. to 3-phenyl-2-ethylindone (22%), m.p. 92—93° (oxime, m.p. 179—180°). $CHPr^aBr{\cdot}CO_2Et$, b.p. 93—94°/25 mm., with $COPh_2$ and Zn in C_6H_6 gives a *substance*, m.p. 112—113°, cyclised by H_2SO_4 to 3-*phenyl*-2-n-*propylindone*, m.p. 72·5—73° (*phenylhydrazone*, m.p. 107—108°). With O_3 and then Zn in AcOH, (**I**) gives the *ozonide* (**II**), m.p. 92—93°, and 2-*propionylbenzil*, m.p. 93°. 83% of (**II**) is obtained in $CHCl_3$ at 0°. (**II**) is very stable, does not explode when heated, and is unaffected by H_2–PtO_2 in EtOH; with 10% KOH–EtOH it gives BzOH (0·95 mol.). With NH_2OH,HCl in boiling C_5H_5N–EtOH, (**II**) gives 1-keto-4-ethyl-2 : 3 : 1-benzoxazine,  (58%), m.p. 117—119°, and with $NHPh{\cdot}NH_2$ at 230—235° gives 3-phenyl-1-ethylphthalazone (2·5%), m.p. 110—112° (Gottlieb, A., 1899, i, 511, m.p. 102°), also obtained in aq. KOH by NH_2OH or $NHPh{\cdot}NH_2$, respectively, from *o*-$COEt{\cdot}C_6H_4{\cdot}CO_2H$ [prep. from *o*-$C_6H_4(CO)_2O$, $EtCO_2H$, and $EtCO_2Na$ at 170°], m.p. 96—97°. The structure of (**I**) is also confirmed by its absorption spectrum [max. at 255 mμ. (log ε 4·765) in 95% EtOH]. R. S. C.

2-Methylene*cyclo*hexanone. K. Dimroth, K. Resin, and H. Zetzsch (*Ber.*, 1940, **73**, [*B*], 1399—1409).—In accordance with Mannich *et al.* (A., 1920, i, 850) *cyclo*hexanone (**I**), CH_2O, and $NHMe_2$,HCl condense smoothly to 2-dimethylaminomethyl*cyclo*hexanone, b.p. 93—94°/11·5 mm. (86% yield), which contrary to these authors gives a *methiodide* (**II**), m.p. 136—137° (2 : 4-*dinitrophenylhydrazone*, m.p. 206—207°), stable when dry. (**II**) decomposes gradually in H_2O. The corresponding quaternary base gives under all conditions as neutral portion a viscous liquid, $C_{14}H_{20}O_2$ (semicarbazone, m.p. 190—191°; oxime, m.p. 120·5°), which is not 2-methylene*cyclo*hexanone, is termed provisionally "dimeric ketone" (**III**), and is possibly (*A*). (**III**) appears identical with the compound obtained by Mannich *et al.* (A., 1928, 300) from 2-piperidinomethyl*cyclo*hexanone (**IV**). Condensation of (**I**) with CH_2O and NH_2Me,HCl proceeds very heterogeneously, giving a most volatile fraction [semicarbazone (**V**), m.p. 195°] which, contrary to Mannich *et al.*, does not consist of 2-methylene*cyclo*hexanone but is 2-methyl*cyclo*hexanone; the less volatile fractions contain some (**III**). The ability of (**V**) to decolorise Br is not evidence of unsaturation but is a general property of the semicarbazones of *cyclo*hexanones and is accompanied by the separation of $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$,HBr. Decomp. of (**IV**), its hydrochloride, or *oxalate*, m.p. 136—137°, under the mildest possible conditions gives only (**III**) and it is improbable that the monomeric ketone can be obtained from such ammonium salts. Energetic dehydrating agents transform 2-hydroxymethyl*cyclo*hexanone (**VI**) into compounds of high mol. wt. Passage over Al_2O_3 (Brockmann) and treatment with $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$,HCl and KOAc leads to a compound, $C_{14}H_{22}O_3$ (**VII**), m.p. 148°, obtained previously by Mannich (*loc. cit.*) and then regarded as a symmetrical ether of (**VI**) but now (unpublished work) considered as allied closely to (**III**). Al_2O_3 in boiling abs. C_6H_6 transforms (**VI**) into (**III**) whilst (**VII**) is obtained from (**VI**) and BzCl in C_5H_5N. Direct condensation of *cyclo*hexanone with CH_2O in dil. aq. alkali gives unchanged material and a viscous yellow oil of high b.p. H. W.


(*A*.)

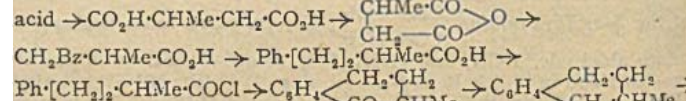
Interaction of diazomethane with 1-keto-1 : 2 : 3 : 4-tetrahydronaphthalene. R. B. Thompson (*J. Amer. Chem. Soc.*, 1944, **66**, 156).—1-Keto-1 : 2 : 3 : 4-tetrahydronaphthalene, CH_2N_2, and Na_2CO_3 in EtOH at 10—15° give 7—8% of non-ketonic material, b.p. 93—96°/0·7 mm., and 6—7% of 3 : 4-*benz*-Δ^3-cyclo*octenone*, m.p. 73—75°, b.p. 103—106°/0·7 mm. (*oximes*, m.p. 164—165° and 89—90°), probably by way of 3 : 4-benz-Δ^3-*cyclo*heptenone which reacts as fast as it is formed. R. S. C.

2-Methyl*meso*benzanthrone and derivatives. D. H. Hey, R. J. Nicholls, and C. W. Pritchett (*J.C.S.*, 1944, 97—100).—$CH_2{:}CMe{\cdot}CHO$ (*oxime*, b.p. 65°/14 mm.) (new methods of prep. given) in dioxan with anthrone in AcOH–H_2SO_4 (*d* 1·53) at 80° gave 2-methyl*meso*benzanthrone (**I**), oxidised (CrO_3) to anthraquinone-1-carboxylic acid (**II**). With MnO_2 and H_2SO_4 (**I**) gave 2 : 2′-dimethyl-3 : 3′-dibenzanthronyl (**III**) and 3-*hydroxy*-2-*methyl*meso*benzanthrone*, m.p. 206—208 (decomp.) [*Me ether*, m.p. 142°; also prepared from $CH_2{:}CMe{\cdot}CO_2Me$ and anthrone, and from 3-*amino*-2-*methyl*meso*benzanthrone* (**IV**), m.p. 232°, by diazotisation and heating]. With KOH–EtOH at 120—130° (**III**) gave 16 : 17-*dimethyldibenzanthrone* (**V**). KOH fusion of (**I**) in presence of glucose or KOAc–$C_{10}H_8$–MnO_2 gave (**V**). With dichloramine-T in AcOH, (**I**) gave 3-*chloro*-2-*methyl*meso*benzanthrone* (**VI**), m.p. 227—228°; 3-*nitro*- (**VII**), m.p. 218—219° [from (**I**) and 88% HNO_3 in $PhNO_2$ at 40—50°; oxidised (CrO_3) to (**II**)], and 3-*bromo*-2-*methyl*meso*benzanthrone* [from (**I**) and from (**IV**)], m.p. 225°, are described. (**VII**) is reduced (Na_2S) to (**IV**). (**VI**) with KOH–EtOH at 150—155° gave 6 : 15-*dimethyliso*dibenzanthrone (**VIII**). (**VI**) with Se, $Ca(OH)_2$, and Cu-bronze in EtOH at 200° gave 2 : 2′-dimethyl-3 : 3′-dibenzanthronyl selenide, m.p. 310—315°, which gave (**VIII**) with KOH–EtOH at 120—130°. (**V**) in boiling $PhNO_2$ (preferably in presence of BaO) gives a product for which the structure



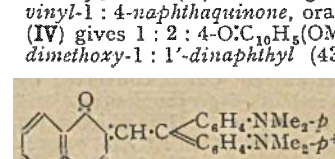
is suggested. D. G.

Synthesis of 2-methyl-1 : 4-naphthaquinone (vitamin-*K*) from benzene and citric or *d*-tartaric acid. P. P. T. Sah and W. Brüll (*Ber.*, 1940, **73**, [*B*], 1430—1432).—The scheme is: citric or tartaric



2-$C_{10}H_7Me$ 2-methyl-1 : 4-naphthaquinone. H. W.

Condensation of naphthaquinones with polar ethylenes. M. Gates (*J. Amer. Chem. Soc.*, 1944, **66**, 124—130).—Condensation readily occurs between $CAr_2{:}CH_2$ and naphthaquinones owing to their electron-donating and -accepting capacities, respectively. The reaction is not catalysed by acids or bases and does not occur in AcOH, in accordance with this explanation. $(p\text{-}NMe_2{\cdot}C_6H_4)_2C{:}CH_2$ (**I**) (1 mol.) and 1 : 4-$O{:}C_{10}H_6{:}O$ (**II**) (2 mols.) condense in C_6H_6, $COMc_2$, or dioxan at room temp. or, best (59% yield), dioxan at 70° (24 hr.) to 2-*ββ-di*-p-*dimethylaminophenylvinyl*-1 : 4-*naphthaquinone* (**III**), purple, m.p. 272—273·5°, and 1 : 4-$C_{10}H_6(OH)_2$ (95%). With Zn dust in Ac_2O–C_5H_5N, (**III**) gives the *quinol diacetate*, yellow, m.p. 230—231° (decomp.). 1 : 2-$O{:}C_{10}H_6{:}O$ (**IV**) condenses very rapidly with (**I**) in warm MeOH, giving 4-*ββ-di*-p-*dimethylaminophenylvinyl*-1 : 2-*naphthaquinone* (83·7%), blue-black, m.p. 199—201° (decomp.) [yellow *quinol diacetate*, m.p. 105·6—106·8°; red *azine*, m.p. 246—247·5°, from *o*-$C_6H_4(NH_2)_2$]. Naphthazarin in C_5H_5N at the b.p. and then 74° or its diacetate in dioxan at 78° with (**I**) gives similarly 5 : 8-*dihydroxy*- (**V**), black, m.p. 306—308° (uncorr.), or 5 : 8-*diacetoxy*-2-*ββ-di*-p-*dimethylaminophenylvinyl*-1 : 4-*naphthaquinone*, blue-black, amorphous, m.p. 261—264° [by hydrolysis gives (**v**), m.p. 307—308° (uncorr.)], respectively, but 1 : 2 : 4-$O{:}C_{10}H_6Me{:}O$ gives a *substance*, $C_{40}H_{40}O_4N_4$, m.p. 298—300° (block; uncorr.). $(p\text{-}OMe{\cdot}C_6H_4)_2C{:}CH_2$, being less polar than (**I**), condenses less readily; with (**II**) in boiling MeOH it gives slowly 2-*ββ-di*-p-*anisylvinyl*-1 : 4-*naphthaquinone*, orange-red, m.p. 211·8—212·3°, but with (**IV**) gives 1 : 2 : 4-$O{:}C_{10}H_5(OMe){:}O$ (8%) and 4 : 4′-*dihydroxy*-3 *dimethoxy*-1 : 1′-*dinaphthyl* (43%), pink, m.p. 277·5—278·8 after slight decomp. (derived phous *quinone*, m.p. 260—262°), which gives the known $(OMe)_4$ compound. Dissolution (reversible) of the highly coloured products in 3N-HCl gives much paler solutions; this is due to resonance of the free quinones, *e.g.*, (**III**) with the form (**VI**), whic


(VI.)

is suppressed by salt-formation. Unless otherwise stated, m.p. are corr. R. S. C.

IV.—STEROLS AND STEROID SAPOGENINS.

Separation of *trans*-œstradiol.—See B., 1944, III, 74.

16-Substituted steroids. I. *iso*Œstriol-*A*. M. N. Huffman and H. H. Darby (*J. Amer. Chem. Soc.*, 1944, **66**, 150—152).—Œstrone benzoate and *iso*-C_5H_{11}·O·NO in KOBu^t–Bu^{t}OH–N_2 at room temp. followed by 0·5N-KOH at room temp. give 16-*oximino-œstrone* (81%), m.p. 214—215° (decomp.), reduced by Zn dust in AcOH–H_2O at AcOH–H_2O at 40—45° and then 120—125° to an impure α-ketol, which with H_2–PtO_2 in 0·5N-NaOH gives *iso*œ*striol*-A (**I**), m.p. 267—269°, $[\alpha]_D^{22.5}$ +88° in EtOH. (**I**) has the same absorption as theelol [œstriol] but is less sol. With Me_2SO_4–NaOH, (**I**) gives a *Me*$_1$ *ether*, m.p. 141—142°, but with Ac_2O–C_5H_5N at 100° gives a *triacetate*, m.p. 152°. R. S. C.

Oxidation of sterols.—See B., 1944, III, 74.

V.—TERPENES AND TRITERPENOID SAPOGENINS.

Hydrocarbon polymerisation and method of determining catalyst activity.—See A., 1944, I, 131.

Reactions of atoms and free radicals in solution. V. Non-coplanar free 1-*apo*camphyl radical. M. S. Kharasch, F. Engelmann, and W. H. Urry (*J. Amer. Chem. Soc.*, 1943, **65**, 2428—2429; cf. A., 1943, II, 150).—*apo*Camphane-1-carboxyl chloride, Na_2O_2, and a little H_2O in Et_2O at −5° to 10° give a relatively stable, cryst. peroxide (**I**), which in CCl_4 at the b.p. (20 hr.) gives 1-chloro*apo*camphane (36%), m.p. 170—171° (Bartlett *et al.*, A., 1940, II, 17, m.p. 154—156°), *apo*camphanyl *apo*camphane-1-carboxylate (50%) [hydrolysed by KOH in $(CH_2{\cdot}OH)_2$], *di*-1-*camphyl* (9%), m.p. 216—217°, *apo*camphane-1-carboxylic acid (**II**) (5%), and C_2Cl_6 [removed from (**II**) by KOH–$(CH_2{\cdot}OH)_2$]. Decomp. of (**I**) yields R· (R = *apo*camphyl) and RCO_2·, and, by interaction of R· with CCl_4, gives CCl_3·; R· is more reactive than CCl_3·. R. S. C.

Triterpenes. LXXXVI. Birch-tar oil. L. Ruzicka, A. G. Boer, and E. Rey (*Helv. Chim. Acta*, 1944, **27**, 183—186).—Technical birch-tar oil is extracted successively with dil. HCl, Na_2CO_3, NaOH, and H_2O, boiled with 10% NaOH–EtOH, and distilled. A fraction b.p. 110—160°/12 mm., is dehydrogenated by S at 180—250° and converted through a series of picrates into additive compounds with s-$C_6H_3(NO_2)_3$, thus leading to the recognition of the presence of 2 : 7-$C_{10}H_6Me_2$, 1 : 2 : 7-$C_{10}H_5Me_3$, and 1 : 2 : 5 : 6-$C_{10}H_4Me_4$. It thus appears that the portions of birch-tar oil which can be dehydrogenated to the methylnaphthalenes are not sesquiterpenes but products of the pyrolysis of betulin. H. W.

Scandol, $C_{30}H_{50}O$, m.p. 161—163°, $[\alpha]_D^6$ +56·9° in $CHCl_3$ (acetate, m.p. 165—168°, $[\alpha]_D^{17}$ +60·5° in $CHCl_3$; benzoate, m.p. 210—212°, $[\alpha]_D^6$ +73·84° in $CHCl_3$).—See A., 1944, III, 383.

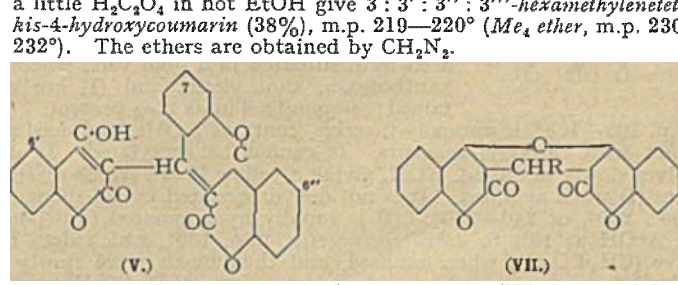
VI.—HETEROCYCLIC.

Synthesis of δ-3 : 4-dicarboxy-2-furyl-*n*-valeric acid and its derivatives. K. Hofmann (*J. Amer. Chem. Soc.*, 1944, **66**, 51—53).—*β*-2-*Furylacrylidenemalonic acid* [prep. from β-2-furylacraldehyde, $CH_2(CO_2H)_2$, and a little piperidine in C_5H_5N], decomp. 190—195°, gives, by hydrogenation (Pd–C; MeOH; 0·1 atm.) and subsequent heating in C_5H_5N at 130—140°, δ-2-*furyl*-n-*valeric acid*, m.p. 42—43° (*anilide*, m.p. 75—76°), which with $(CO_2Et)_2$ at 100° gives an adduct, hydrogenated (Pd-black) in EtOAc to δ-1 : 4-epoxy-2 : 3-dicarbethoxy-Δ^3-*cyclo*hexenyl-*n*-valeric acid. At 190—200°/16 mm. this gives C_2H_4 and δ-3 : 4-dicarbethoxy-2-furyl-*n*-valeric acid, hydrolysed by 5N-KOH at the b.p. to δ-3 : 4-*dicarboxy*-2-*furyl*-n-*valeric acid*, m.p. 188—190° (Et_2 ester, b.p. 165—166°/0·02 mm.; absorption spectrum resembles that of furan-3 : 4-dicarboxylic acid), and converted by $SOCl_2$ into the acid chloride, b.p. 177—178°/0·02 mm. Thence are obtained δ-3 : 4-dicarbethoxy-, b.p. 210—211°/0·02 mm., and δ-3 : 4-*dicarboxy*-2-*furyl*-n-*valeropiperidide*, m.p. 132—133°. M.p. are corr. R. S. C.

Synthesis of two stereoisomeric 3 : 4-diaminotetrahydro-2-furyl-*n*-valeric acids. K. Hofmann (*J. Amer. Chem. Soc.*, 1944, **66**, 157).—δ-2-Furyl-*n*-amyl alcohol (*α-naphthylurethane*, m.p. 58—59°) by condensation with $(CO_2Et)_2$ and then high-pressure hydrogenation gives δ-3 : 4-dicarbethoxytetrahydro-2-furyl-*n*-amyl alcohol, which yields *dihydrazides*, m.p. 208—211° and 177—180°, and thence successively (Curtius) ε-3 : 4-*di*(*carbethoxyamino*)*tetrahydro*-2-*furyl*-n-*amyl alcohols*, m.p. 110—113° and 128—130°, (CrO_3–AcOH) the derived n-*valeric acids*, m.p. 118—124° and 157—159°, and [conc. Ba(OH)$_2$]– δ-3 : 4-diaminotetrahydro-2-furyl-*n*-valeric acids (*Bz*$_2$ derivatives of the *Me* esters, m.p. 183—186° and 171—172°), respectively. R. S. C.

4-Hydroxycoumarins. I. Synthesis of 4-hydroxycoumarins. A. Stahmann, I. Wolff, and K. P. Link. **II. Condensation of aldehydes with 4-hydroxycoumarins.** W. R. Sullivan, C. F. Huebner M. A. Stahmann, and K. P. Link. **III. Dehydration of the aldehyde condensation products.** C. F. Huebner, W. R. Sullivan, M. A. Stahmann, and K. P. Link (*J. Amer. Chem. Soc.*, 1943, **65**, 2285—2287, 2288—2291, 2292—2296).—I. *o*-OAc·C_6H_4·CO_2Me [prep. from *o*-OH·C_6H_4·CO_2Me (**I**) by Ac_2O and a little H_2SO_4 at 40°; 95% yield], m.p. 47—49°, and Na give >13% of 4-hydroxycoumarin (**II**) by the method of Pauly *et al.* (A., 1915, i, 146), but 22% is obtained in liquid paraffin at 240—250°; other alkaline condensing agents offer no advantage; by-products include *o*-OH·C_6H_4·CO_2H, PhOH, PhOMe, MeOAc, AcOH, and acidic substances separating at pH 5·5—6 (and thus removable). Pure (**II**) has m.p. 214—216° (lit. 204—206°). *Me* O-*propionylsalicylate*, b.p. 141—142°/9 mm., is obtained as above. RCOCl and (**I**) at the b.p. give *Me* O-n- (81%), b.p. 155—156°/12 mm., and O-iso-*butyryl*- (68%), b.p. 140—143°/6 mm., O-n- (65%), b.p. 158—159°/8 mm., and O-iso-*valeryl*- (71%), b.p. 151—152°/8 mm., O-n-*hexoyl*- (56%), b.p. 173—174°/9 mm., O-n-*heptoyl*- (73%), b.p. 181—182°/9 mm., O-*stearyl*- (47%), m.p. 41—43°, b.p. 226—230°/0·05 mm., O-*β-phenylpropionyl*- (74%), b.p. 197—201°/5 mm., and *O*-phenylacetyl- (63%), m.p. 59—60° (lit. 50°), -*salicylate*. With Na in liquid paraffin at 240—250° these esters give 4-hydroxy-3-methyl- (28%), m.p. 227—228° (lit. 230°), -3-*ethyl*- (28%), m.p. 155—156°, -3-n- (32%), m.p. 134—135°, and -3-iso-*propyl*- (25%), m.p. 172—174°, -3-n-*butyl*- (26%), m.p. 158—159°, -3-n-*amyl*- (30%), m.p. 137—139°, -3-*hexadecyl*- (21%), m.p. 96—97°, -3-phenyl- (25%), m.p. 234—235° (lit. 236°), and -3-benzylcoumarin (22%), m.p. 202—205°. The 3-alkylcoumarins have slight anticoagulant activity, increasing with the size of the alkyl and being greater for 3-aryl derivatives.

II. *o*-OH·C_6H_4·CHO (**III**) (1 mol.) and (**II**) (1 mol.) in EtOH at the b.p. (10 min.) and then 25° (1 hr.) give 2 : 5-*diketo*-3-*salicylidene*-*chroman* (**IV**) (20%), yellow, m.p. 175°, and other products. 1 mol. each of (**IV**) and (**III**) in boiling EtOH (5 hr.) give colourless 4-4′-*hydroxycoumarinylcoumarino*-4′ : 3′-2 : 3-1 : 4-*benzpyran* (**V**) (76·3%), m.p. 245° (decomp.), also obtained (44%) from (**III**) (0·031) and (**II**) (0·019 mol.) in boiling EtOH (1 hr.) or (73·2%) by boiling (**IV**) in EtOH for 13·5 hr. The structure of (**V**) is proved by electrometric titration (one deflexion; at pH 5·7), by its anticoagulant activity, and conversion by NH_2Ph at 180° into the anil of (**II**). Similar reactions of (**II**) with 2 : 4 : 1-$(OH)_2C_6H_3$·CHO lead to the 7-*OH*-derivative, m.p. 251° (decomp.) [*acetate*, m.p. 236° (decomp.); *Me ether*, m.p. 301—304° (decomp.)], of (**V**) and 2 : 4-*diketo*-3-2′ : 4′-*dihydroxybenzylidenechroman*, decomp. 224°. 4-Hydroxy-6-methylcoumarin and (**IV**) in hot EtOH (5 hr.) give the 6′- and 6″-*Me* derivative (61·7%), m.p. 277—278° (decomp.), of (**V**). Simple bis-condensation of RCHO (0·5—0·7) and (**II**) (1 mol.) in boiling EtOH leads to 3 : 3′-ethylidene- (67%), m.p. 176—178° (lit. 165°), 3 : 3′-*propylidene*- (69%), m.p. 144—145° (*Me*$_2$ *ether*, m.p. 129°), 3 : 3′-n- (86%), m.p. 123—124° (*Me*$_2$ *ether*, m.p. 118—120°), and 3 : 3′-iso-*butylidene*- (78%), m.p. 199—200° (*Me*$_2$ *ether*, m.p. 214—215°), 3 : 3′-n- (75%), m.p. 113° (*Me*$_2$ *ether*, m.p. 129—130°), and 3 : 3′-iso-*pentylidene*-, m.p. 142—143° (*Me*$_2$ *ether*, m.p. 148°), 3 : 3′-n-*hexylidene*- (prep. in presence of 0·25 mol. of $AlCl_3$) (18%), m.p. 104—105° (*Me*$_2$ *ether*, m.p. 113—115°), 3 : 3′-*benzylidene*- (91%), m.p. 228—229° (*Me*$_2$ *ether*, m.p. 181—183°), 3 : 3′-*β-phenylethylidene*- (40%), m.p. 175—177°, 3 : 3′-*γ-phenylpropylidene*- (85%), m.p. 197—198° (*Me*$_2$ *ether*, m.p. 170—173°), 3 : 3′-p-*anisylidene*- (80%), m.p. 242° (decomp.) (*Me*$_2$ *ether*, m.p. 170—171°), 3 : 3′-4″-*hydroxy*-3″-*methoxybenzylidene*- (93%), m.p. 213—215°, 3 : 3′-3″ : 4″-*methylenedioxybenzylidene*- (67%), m.p. 256° (decomp.), 3 : 3′-p-*dimethylaminobenzylidene*- (76%), m.p. 210° (decomp.), and 3 : 3′-*carboxymethylene*- (prep. from CHO·CO_2H in boiling H_2O; 76%), m.p. 244—245° (*Me*$_2$ *ether Me* ester, m.p. 160—161°), -*bis*-4-*hydroxycoumarin*. $[CH_2]_4(CHO)_2$, (**II**), and a little $H_2C_2O_4$ in hot EtOH give 3 : 3′ : 3″ : 3‴-*hexamethylenetetrakis*-4-*hydroxycoumarin* (38%), m.p. 219—220° (*Me*$_4$ *ether*, m.p. 230—232°). The ethers are obtained by CH_2N_2.



III. 3 : 3′-Methylenebis-4-hydroxycoumarin (**VI**) is not dehydrated by Ac_2O–C_5H_5N (cf. A., 1941, II, 202) but with $KHSO_4$ at 270°, red P–I–AcOH–H_2O at 155—165°, or $(OPh)_2POCl$–C_5H_5N at room temp. gives 4 : 4′-*epoxy*-3 : 3′-*methylenebiscoumarin* [3 : 2-5 : 6-*di*-(3′ : 4′-*coumarino*)-4-*pyran*] [(**VII**), R = H], m.p. 321—323° (decomp.). (**VII**) are obtained from 3 : 3′-alkylidene- and 3 : 3′-arylidene-analogues of (**VI**) by Ac_2O–C_5H_5N at room temp., there being thus obtained derivatives of (**VII**) in which R = *Me*, m.p. 322—323° (decomp.), *Et*, m.p. 292—294° (decomp.), *Pr*$^\alpha$, m.p. 246° (decomp.), *Pr*$^\beta$, m.p. 303°, *Bu*$^\alpha$, m.p. 231°, *Bu*$^\beta$, m.p. 290°, n-*amyl*, m.p. 182°, *Ph*, m.p. 393—395°, CH_2Ph, m.p. 385° (decomp.), *Ph*·$[CH_2]_3$, m.p. 243—245°, p-*anisyl*-, m.p. 345° (decomp.), 3 : 4 : 1-

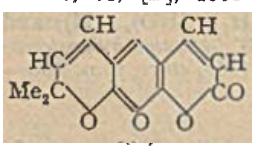
OMe·C$_6$H$_3$(OAc) (from 3 : 3′-*vanillylidenebis-4-hydroxycoumarin* after acetylation thereof), m.p. 288—289°, and 3 : 4 : 1-*CH$_2$O$_2$.C$_6$H$_3$*, m.p. 355—356°. Dehydration is the easier the larger is R. Mono-*O*-Me, -Bz, and PO$_3$Me$_2$ derivatives of (**VI**) give (**VII**) by loss of MeOH, BzOH, and Me$_2$HPO$_4$, respectively. Diacyl derivatives of (**VI**) and its analogues resist dehydration so that Ac$_2$O–C$_5$H$_5$N probably effects it by way of the monoacetate. PCl$_5$ and (**VI**) in C$_6$H$_6$ give a mixture, converted by hot MeOH into the 4-*PO$_3$Me$_2$* derivative (**VIII**), m.p. 186—187°, of (**VI**); this is hydrolysed to (**VI**) by hot 3% HCl–MeOH but is converted in 94—97% yield into (**VII**), R = H, by hot NaOMe–MeOH or aq. KOH at 25° or, less well, by heating at 200°. 0·5N-NaOMe converts (**VII**), R = H, into the 4-*Me ether* (**IX**), m.p. 171—172°, of (**VI**); with CH$_2$N$_2$ this gives the 4 : 4′-Me$_2$ ether but at 180° regenerates (**VII**), R = H. The *Na$_1$* salt (prep. by 1 equiv. of hot, aq. 0·05N-NaOH) of (**VI**) gives the Ag$_1$ salt, which with a deficiency of BzCl and CaSO$_4$ in C$_6$H$_6$ at room temp. gives the 4-*Bz* derivative, m.p. 225—229°; at > the m.p. this gives BzOH and (**VII**), R = H, with 1 mol. of NaOMe–MeOH at 65° gives a mixture of (i) (**VII**), R = H, and NaOBz with (ii) MeOBz and the Na salt of (**VI**). CH$_2$N$_2$–Et$_2$O converts (**VIII**) into the 4-*Me ether* 4′-*PO$_3$Me$_2$* derivative, m.p. 140—141°, which is also obtained from (**IX**) by POCl$_3$–C$_5$H$_5$N at 0° and then MeOH. The epoxy-ring of (**VII**) is stable to aq. alkali or acid or boiling NH$_2$Ph, but is opened by NaOMe (see above); fusion with KOH gives a small amount of *o*-OH·C$_6$H$_4$·CO$_2$H. (**VII**) give no colour with FeCl$_3$, give a yellow to orange solution in conc. H$_2$SO$_4$, and have no anticoagulant action. Prep. of (**VII**), R = Ph, by dehydration by boiling 58% HBr–AcOH is described. The 4-*Et$_1$ ether*, m.p. 163—166°, of (**VI**) and 3 : 3′-*ethylidenebis-4-hydroxycoumarin* 4-*Me$_1$ ether*, m.p. 154—155°, are also prepared. R. S. C.

Egonol. XIII. 4-Bromo- and 3-nitro-acetylegonol and a new degradation of the 3-nitrofuran ring. S. Kawai, T. Nakamura, Y. Kitazawa, and K. Komatsu (*Ber.*, 1940, **73**, [*B*], 1328—1337).—3-Nitroacetylegonol (**I**) is converted by boiling 2% KOH–EtOH into KNO$_2$, piperonylic acid, *α-keto-β-ethoxy-α*-3 : 4-*methylenedioxyphenyl-β*-2-*hydroxy*-3-*methoxy*-5-*γ-hydroxy*-n-*propylphenylethane*, m.p. 147° (non-cryst. oxime), and an oily material not identical with styraxinolaldehyde and from which the *di*-p-*nitrobenzoate* of 2-methoxy-6-ethoxymethyl-4-*γ*-hydroxy-*n*-propylphenol, m.p. 130—130·5°, is derived. (**I**) and boiling 1·7% KOH–MeOH afford only 3-nitroegonol, m.p. 151°. 4-*Bromo*-3-*nitroacetylegonol* (**II**), m.p. 139°, is obtained from (**I**) and Br in AcOH at room temp. or by addition of HNO$_3$ (*d* 1·4) to 4-bromoacetylegonol in well-cooled AcO. (**II**) is transformed by boiling NaOEt–EtOH into 4-*bromo*-3-*nitro*-2 *hydroxy*-2 : 3-*dihydroegonol*, m.p. 166·5°, converted by boiling 2N. aq. KOH into 5-*bromo*-2-*methoxy*-6-*hydroxymethyl*-4-*γ-hydroxy*-n-*propylphenol*, m.p. 129·5° (*tri*-p-*nitrobenzoate*, m.p. 189·5°), which is methylated and oxidised (KMnO$_4$ in COMe$_2$) to 2-bromo-4 : 5-dimethoxybenzene-1 : 3-dicarboxylic acid (**III**), identified as the *diphenacyl* ester (**IV**), m.p. 153·5°. 6-Bromovanillin is transformed by CH$_2$:CH·CH$_2$Br and dry K$_2$CO$_3$ in boiling anhyd. COMe$_2$ into the *allyl ether*, m.p. 89°, isomerised at 230—250° to 6-*bromo*-5-*allylvanillin*, m.p. 134°. This is transformed into the *Me ether*, m.p. 63—64°, which is oxidised to (**III**), identified as (**IV**). H. W.

Tetrahydrodibenzpyran.—See B., 1944, III, 74.

Mechanism of a photo-disproportionation reaction [13-phenyldibenzoxanthenium perchlorate].—See A., 1944, I, 110.

Natural coumarins. LIV. Constitution of luvangetin. E. Spath, P. K. Bose, H. Schmid, E. Dobrovolny, and A. Mookerjee (*Ber.*, 1940, **73**, [*B*], 1361—1368).—Luvangetin (**I**) is *A*. The finely-divided ripe fruits of *Luvanga scandens*, Ham., are extracted with Et$_2$O, the extract is subjected to the lactone separation, and the total non-phenolic coumarins are separated by distillation in a high vac., whereby xanthotoxin, xanthyletin, and (**I**) are obtained; *iso*pimpinellin is also present. (**I**), m.p. 108—109°, is optically inactive, contains 1 OMe, and does not react with carbonyl reagents. It cannot be acetylated. It dissolves slowly in dil. aq. KOH, giving a yellow K salt which regenerates (**I**) when acidified. It is not dehydrogenated by Pd-sponge at 180°, 200°, or 240—250°. (**I**) is rapidly hydrogenated (Pd-sponge in AcOH at 16°) to *dihydroluvangetin*, m.p. 130°, which does not give (CH$_2$·CO$_2$H)$_2$ when oxidised, and then much more slowly to *tetrahydroluvangetin*, m.p. 99°, which gives (CH$_2$·CO$_2$H)$_2$ when treated with HNO$_3$ (*d* 1·4). (**I**) is converted by successive treatments with red P and 48% HBr at 150°, CH$_2$N$_2$ in MeOH–Et$_2$O, NaOH and Me$_2$SO$_4$, and 3% aq. NaOH into 2 : 3 : 4 : 1-(OMe)$_3$C$_6$H$_2$·CO$_2$H. Ozonisation of (**I**) and decomp. of the ozonide by boiling H$_2$O leads to 7-*hydroxy*-8-*methoxycoumarin*-6-*aldehyde*, m.p. 197·5—198·5° (vac.), also obtained by ozonisation of xanthotoxin. OH·CMe$_2$·CO$_2$H is obtained by oxidation of (**I**) by KMnO$_4$. H. W.



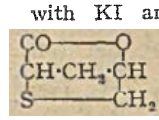
Tetramethylpopulnetin, m.p. 164—166°.—See A., 1944, III, 384.

Thiophan compounds. II. Thiophan-3-one. P. Karrer and H. Schmid. **Thiophan compounds. III.** H. Schmid. **Thiophan compounds. IV.** P. Karrer and F. Kehrer (*Helv. Chim. Acta*, 1944, **27**, 116—123, 124—127, 127—142, 142—151).—II. I·[CH$_2$]$_2$·COCl (**I**), b.p. 71—75°/11 mm., obtained from I·[CH$_2$]$_2$·CO$_2$H and SOCl$_2$ in 90% yield, is converted by CH$_2$N$_2$ in Et$_2$O followed by HCl into *CH$_2$Cl β-iodoethyl ketone*, m.p. 54—55°, which can be kept only when pure. Gradual addition of Na$_2$S to a solution of it in much EtOH leads to *thiophan*-3-*one* (**II**), b.p. 84—85°/24 mm., separated as the *semicarbazone*, m.p. 191—192° (decomp.). Smaller yields are obtained if (**I**) is replaced by Cl·[CH$_2$]$_2$·COCl probably because of the too great differences in the reactivities of the Cl atoms. Cl·[CH$_2$]$_2$·CO$_2$Na, SH·CH$_2$·CO$_2$H, and KOH in boiling H$_2$O afford CO$_2$H·CH$_2$·S·[CH$_2$]$_2$·CO$_2$H, m.p. 94° (yield nearly quant.), converted by HCl–EtOH into the *Et$_2$* ester, b.p. 148—150°/10 mm., which is ring-closed by NaOEt or NaNH$_2$ to Et 3-ketothiophancarboxylate (**III**), b.p. 123—127°/11 mm. This gives a red-violet colour with FeCl$_3$ and is hydrolysed and decarboxylated by boiling 10% H$_2$SO$_4$ to (**II**). Methylation and subsequent decarboxylation of (**III**) gives 4-methylthiophan-3-one (**IV**), isolated as the *semicarbazone*, decomp. 192·5—193·5°.

II. SH·[CH$_2$]$_2$·CO$_2$H is converted by boiling abs. EtOH–H$_2$SO$_4$ under CO$_2$ into *Et β-thiolpropionate*, b.p. 77·5°/20 mm., which is transformed by CHMeBr·CO$_2$Et and NaOEt in abs. EtOH into *Et$_2$ sulphido-α-propionate-β-propionate*, b.p. 149—153°/10·5 mm. This is cyclised by NaNH$_2$ in abs. EtOH at 40—50° to *Et* 3-*keto*-2-*methylthiophan*-4-*carboxylate*, b.p. 125—128° (bath)/9 mm., which gives a marked red-violet colour with FeCl$_3$. This is hydrolysed and decarboxylated by boiling 10% H$_2$SO$_4$ to 2-*methylthiophan*-3-*one*, b.p. 90—100° (bath)/11 mm. [*semicarbazone*, m.p. 183—184° (decomp.)], thus indirectly establishing the structure of (**IV**). The isolation of two isomeric *phenylhydrazones*, m.p. 141·5—142·5° and 167° respectively, proves that (**III**) is a mixture of Et 3-ketothiophan-2- and -4-carboxylate.

III. Br·[CH$_2$]$_4$·Br, b.p. 78—81°/11 mm., obtained in 58% yield from [CH$_2$]$_4$(CO$_2$Ag)$_2$ and Br in CCl$_4$, is converted by NaOMe in MeOH–C$_6$H$_6$ into *Me δ-bromo*-n-*butyl ether*, b.p. 70—82°/34—35 mm., which is transformed with aid of CHNa(CO$_2$Et)$_2$ into *Et$_1$ δ-methoxybutylmalonate*, b.p. 146°/8·5 mm., hydrolysed by alkali to the non-cryst. *acid*. This is converted by Br in Et$_2$O–CCl$_4$ into *α-bromo-δ-methoxybutylmalonic acid*, m.p. 122—123° (decomp.), which passes at 120—130°/vac. into *α-bromo-ε-methoxyhexoic acid*, b.p. 124—128° (bath)/0·08 mm. The *Et* ester, b.p. 128—132°/10 mm. (corresponding *Me* ester, b.p. 120—124°/10 mm.), is condensed with SH·[CH$_2$]$_2$·CO$_2$Et by NaOEt–EtOH to *Et$_2$ sulphido-β-propionate α-ε-methoxyhexoate*, b.p. 145—148°/0·02 mm., cyclised by NaOMe in PhMe at 45—50° to *Et* 3-*keto*-2-*δ-methoxy*-n-*butylthiophan*-4-*carboxylate* (**V**), b.p. 115° (bath)/0·01 mm. [*oxime* (**VI**), b.p. 145—155° (bath)/0·02 mm.; non-cryst. *phenylhydrazone*], which gives a marked red-violet colour with FeCl$_3$ in EtOH–H$_2$O. (**VI**) is reduced by Al–Hg in moist Et$_2$O to *Et* 3-*amino*-2-*δ-methoxy*-n-*butylthiophan*-4-*carboxylate*. (**V**) is hydrolysed and decarboxylated by boiling H$_2$O–AcOH–H$_2$SO$_4$ under N$_2$ to 2-*δ-methoxy*-n-*butylthiophan*-3-*one* (**VII**), b.p. 102—103°/0·05 mm. This is oxidised by Br in aq. MeOH containing CaCO$_3$ to 4-hydroxy-2-δ-methoxy-*n*-butylthiophan-3-one, which strongly reduces Ag$_2$O–NH$_3$ but could not be purified; it is converted by NH$_2$OH,HCl and KOAc in H$_2$O at 40° into 2-*δ-methoxy*-n-*butylthiophan*-3 : 4-*dionedioxime* (**VIII**), m.p. 189° [corresponding *phenylosazone* (**IX**), m.p. 141° (decomp.)]. (**VII**) could not be converted into 3 : 4-diamino-2-δ-methoxy-*n*-butylthiophan. Reduction of (**VII**) by Na–Hg in EtOH–AcOH at ~50° leads to 4(3)-*amino*-3(4)-*hydroxy*-2-*δ-methoxy*-n-*butylthiophan*, m.p. 107—108°, which is very hygroscopic and avidly absorbs atm. CO$_2$; under completely anhyd. conditions the product is non-homogeneous. Na in boiling EtOH reduces (**VIII**) to an oil with 8·6% N. H$_2$ at 70°/24 atm. in abs. EtOH containing Raney Ni does not attack (**VIII**). With Al–Hg and H$_2$O in EtOH–Et$_2$O (**VIII**) appears to give 3(4)-*amino*-2-*δ-methoxy*-n-*butylthiophan*, m.p. 157°, softens at 151°. Attempted reduction of (**IX**) by Na–Hg in EtOH–AcOH gives ill-defined results. *Me$_2$ sulphido-β-α-methoxypropionate-α-ε-methoxyhexoate*, b.p. 140—145° (bath)/0·005 mm., is cylised by NaOEt in PhMe at 18° and then at 40° to a non-homogeneous product, hydrolysed and decarboxylated to (**VII**). (**II**) is converted by C$_5$H$_{11}$·O·NO and conc. HCl into 2 : 4-*dioximinothiophan*-3-*one*, decomp. 210°, becoming increasingly discoloured at >170°. (**III**) couples with *p*-NO$_2$·C$_6$H$_4$·N$_2$Cl in aq. EtOH to a mixture, m.p. 145—150°, of Et 2-*p*-nitrobenzeneazo-3-ketothiophan-4-carboxylate and Et 4-*p*-nitrobenzeneazo-3-ketothiophan-2-carboxylate with some *Et* 4-*p-nitrobenzeneazo*-3-*ketothiophan*-4-*carboxylate*, m.p. 168—169°. Reduction of these dyes gives *p*-C$_6$H$_4$(NH$_2$)$_2$ as sole recognisable product.

IV. CHBr·CH$_2$>CO———O>CH·CH$_2$Cl is converted by successive treatment with KI and Na$_2$S into 4-*hydroxythiophan*-2-*carboxylactone* (**X**), m.p. 60·5°, in very poor yield. [CH$_2$]$_4$(CO$_2$H)$_2$ transformed by successive treatments with SOCl$_2$, Br at 60° with irradiation, and EtOH into *Et$_2$ α-bromoglutarate*, b.p. 136—144°/11 mm., which is condensed with *Et β-bromopropionate*, b.p. 77—78°/20 mm., to *Et$_3$ sulphido-β-propionate-α-glutarate*, b.p. 150—153°/0·02 mm., which is cyclised by NaOEt in PhMe at room



(**X**.)

temp. and then at 55—60° to Et_2 3-*ketothiophan*-4-*carboxylate*-2-β-*propionate* (**XI**), b.p. 130—133°/0·04 mm., hydrolysed and decarboxylated by boiling 10% H_2SO_4 to 3-*ketothiophan*-2-β-*propionic acid* (**XII**), b.p. 132—135° (bath)/0·03 mm., m.p. 51° (*Me* ester). Attempts to convert (**XII**) into its :N·OH derivative were unsuccessful. (**XI**) couples with *p*-$NO_2{\cdot}C_6H_4{\cdot}N_2Cl$ to (?) Et_2 4-p-*nitrobenzeneazo*-3-*ketothiophan*-4-*carboxylate*-2-β-*propionate*, which could not be reduced to the NH_2-ketone. Cautious bromination of (**XII**) in presence of $CaCO_3$ gives the unstable 4-Br-compound and thence 4-*hydroxy*-3-*ketothiophan*-2-β-*propionic acid*, m.p. 129—130° (slight decomp.). This is converted by NH_2OH,HCl and KOAc at 100° into 3 : 4-*dioximinothiophan*-2-β-*propionic acid*, decomp. 185—189° (corresponding *phenylosazone*, decomp. 112—115°), which could not be satisfactorily reduced to the diamine. (**XI**) is transformed by Br in light petroleum followed by boiling 10% H_2SO_4 into 3 : 4-*dihydroxythiophen*-2-β-*propionic acid*, decomp. 194—197°, which gives a blue-green colour with $FeCl_3$. H. W.

Synthesis of 3-alkylpiperidones. C. F. Koelsch (*J. Amer. Chem. Soc.*, 1943, **65**, 2458—2459).—CH_2:CH·CN and $CHNa(CO_2Et)_2$ in EtOH at 40° and then 65° give *Et* γ-*cyano*-α-*carbethoxy*-n-*butyrate* (40—45%), b.p. 175—180°/25 mm., which is hydrogenated and cyclised by H_2–Raney Ni (no solvent) at 100°/2000 lb. to yield *Et* 2-*piperidone*-3-*carboxylate* (57%), m.p. 78—79°, b.p. 205—215°/15 mm. With NaOEt and then EtI in boiling EtOH, this gives *Et* 3-*ethyl*-2-*piperidone*-3-*carboxylate* (66%), m.p. 46—49°, b.p. 190—198°/12 mm., hydrolysed by aq. KOH at 105° to the syrupy acid, which, when distilled, yields 3-*ethyl*-2-*piperidone*, m.p. 66—68°, b.p. 149°/15 mm. (reduced by Na–BuOH to 3-ethylpiperidine). Adding CH_2:CH·CO_2Me (**I**) to CN·CHNa·CO_2Et (**II**) in EtOH and then heating yields Et_2 α-*cyanoglutarate*, b.p. 180°/25 mm., which with H_2–Raney Ni in EtOH at 140°/2000 lb. gives *Et* 2-*piperidone*-5-*carboxylate*, m.p. 62—64°, b.p. 163°/2 mm. (partial decomp. at 20 mm.). Adding CH_2PhCl to the Na derivative from (**I**) and (**II**) in EtOH and then boiling gives Et_2 α-*cyano*-α-*benzylglutarate*, b.p. 187—195°/2 mm., converted by H_2–Raney Ni in EtOH at 165°/2000 lb. into *Et* 5-*benzyl*-2-*piperidone*-5-*carboxylate*, $+H_2O$, m.p. 64—68°, which is hydrolysed by 2% NaOH to the corresponding *acid*, m.p. 221—222°. R. S. C.

Synthesis of 4-phenylpiperidines. C. F. Koelsch (*J. Amer. Chem. Soc.*, 1943, **65**, 2459—2460).—$CO_2Et{\cdot}CH_2{\cdot}CHPh{\cdot}CH(CN){\cdot}CO_2Et$ (from CHPh:CH·CO_2Et and CN·CHNa·CO_2Et), b.p. 172—175°/2 mm., with H_2–Raney Ni at 140°/2000 lb. gives *Et* 4-*phenyl*-2-*piperidone*-5-*carboxylate* (67%), m.p. 102—103° (crude, 91—94°, ? stereoisomerides) (derived *acid*, m.p. 214—215°), which with Na–BuOH gives 4-phenylpiperidine-3-carboxylic acid [*hydrochloride* (**I**), yellow at 150°, sinters 250°, m.p. 257—259° (gas)]. With 40% CH_2O at 100°, (**I**) gives 4-*phenyl*-1-*methylpiperidine*-3-*carboxylic acid hydrochloride*, m.p. 219—222° (*Et* ester *hydrochloride*, m.p. 171—173°). *Et* γ-*cyano*-α-*carbethoxy*-β-*phenyl*-n-*butyrate* [from CHPh:CH·CN, $CH_2(CO_2Et)_2$, and NaOEt in boiling EtOH; 83% yield], m.p. 43—45°, b.p. 190—195°/0·5 mm., with H_2–Raney Ni at 155°/2000 lb. gives Et 4-phenyl-2-piperidone-3-carboxylate, a syrup, and 4-*phenyl*-2-*piperidone* (**II**), m.p. 137—139°. Na–BuOH reduces (**II**) to 4-phenylpiperidine, m.p. 57—60° (lit., 57—58°), b.p. 137—147°/21 mm. (and a base, m.p. 137°, b.p. 160—220°/18 mm.), the hydrochloride, sinters 110°, m.p. 164—165° (slow heating), 150° (decomp.; immediate), of which with an excess of aq. CH_2O at 100° gives 4-phenyl-1-methylpiperidine, b.p. 138—140°/17 mm. (*hydrochloride*, m.p. 185—187°), and (?) methylenebis-4-phenylpiperidine, m.p. 101—103°. R. S. C.

Two syntheses of β-1-benzoyl-4-piperidylpropionic acid. C. F. Koelsch (*J. Amer. Chem. Soc.*, 1943, **65**, 2460—2465).—Epichlorohydrin with H_2SO_4 in boiling MeOH gives OMe·CH_2·CH(OH)·CH_2Cl (**I**) (75—85%), b.p. 75—78°/12 mm., and $CH_2Cl{\cdot}CH(OH){\cdot}CH_2{\cdot}O{\cdot}SO_3H$ (deliquescent *Na* salt). With aq. NaCN at 44—46°, rising later to 50°, (**I**) gives β-*hydroxy*-γ-*methoxy*-n-*butyronitrile* (**II**) (77—92%), b.p. 133°/18 mm., which is converted into γ-*methoxycrotononitrile* (**III**), b.p. 175—185°, by distillation from K_2CO_3 (70% yield) or by acetylation (boiling Ac_2O) into β-*acetoxy*-γ-*methoxy*-n-*butyronitrile* (96%), b.p. 128—130°/21 mm. (hydrolysed by boiling 0·1N-NaOH in 1 min.), which yields (**III**) (83%) when distilled from a little KOAc. $CH_2(CO_2Et)_2$ or CN·CH_2·CO_2Et does not condense with (**II**), but $CHNa(CO_2Et)_2$ and (**III**) in hot EtOH give *Et* γ-*cyano*-α-*carbethoxy*-β-*methoxymethyl*-n-*butyric acid* (77%), b.p. 180—185°/20 mm., which with H_2–Raney Ni in 95% EtOH at 140—155°/2500 lb. gives *Et* 4-*methoxy*-2-*piperidone*-3-*carboxylate* (60%), b.p. 220—225°/30 mm., whence hydrolysis (aq. KOH) and distillation yields 4-*methoxymethyl*-2-*piperidone* (**IV**) (83%), m.p. 59—62°, b.p. 179—181°/21 mm. Na (4 atoms utilised)–BuOH reduces (**IV**) to 4-*methoxymethylpiperidine* (60—68%), hygroscopic, m.p. ~0°, b.p. 80—81°/27 mm. [*picrate*, m.p. 146—148°; *hydrochloride*, m.p. 150°; *hydrobromide* (**V**), m.p. 143°; *p*-$NO_2{\cdot}C_6H_4{\cdot}CO$ derivative, m.p. 84—86°; *NO*-derivative, b.p. 158—160°, with Zn–H_2SO_4 at 55—60° gives the 1-NH_2-derivative, b.p. 100—110°/25 mm. (*hydrobromide*, m.p. 102—104°)]. (**V**) is converted by boiling 48% HBr in 10 min. into 4-*hydroxymethyl*-, m.p. 150—151°, and in 7 hr. into impure 4-bromomethyl-piperidine hydrobromide (**VI**), hygroscopic, identified by conversion by 5% NaOH into 1-azadi*cyclo*[1, 2, 2]heptane. 1-*Benzoyl*-4-*bromomethylpiperidide* (**VII**) [prep. from, best, pure (**VI**) by BzCl–aq. Na_2CO_3 at 0°; 73%], m.p. 88—90°, does not condense with the *Na* derivative of Et β-keto-β-4-quinolylpropionate [sulphate, m.p. 150° (decomp.); *picrate*, m.p. 160—163°] in EtOH and in Et_2CO_3 gives tars, but with the *Ag* derivative at 100° gives 1-*benzoyl*-4-*piperidylmethyl cinchonate*, m.p. 132—133° (*picrate*, sinters 165°, m.p. 170—172°), also obtained from (**VII**) and Ag cinchonate at 100°. Et cinchonate picrate, m.p. 183—185°, is described. $CHNa(CO_2Et)_2$ and (**VII**) (28 g.) in hot EtOH give a syrupy ester, which, when hydrolysed by NaOH–H_2O–EtOH and then heated at 185°, gives β-1-*benzoyl*-4-*piperidylpropionic acid* (**VIII**) (5·2 g.), m.p. 145—147°, and its Et ester (7·7 g.), b.p. 240—245°/6 mm. Pyridine-4-carboxylic acid (prep. from 4-methylpyridine by boiling aq. $KMnO_4$ in 45—62·4% yield) and H_2SO_4–EtOH give the Et ester (67%), which with NaOEt and EtOAc in boiling EtOH–Et_2O gives Et β-keto-β-4-pyridylpropionate (53·5%). With H_2–Raney Ni in EtOH at 100°/2200 lb. this gives Et β-4-pyridylhydracrylate, an oil (*hydrochloride*, sinters 153°, m.p. 155—157°), hydrolysed by hot HCl to β-4-*pyridylhydracrylic acid*, sinters 193°, m.p. 201—202° [purified by way of the *Cu* salt, m.p. 207—208° (decomp.); *hydrochloride*, sinters 170°, m.p. 173—175°]. 1 : 1 (vol.) H_2SO_4–H_2O at the b.p. then gives β-4-pyridylacrylic acid, brown at 190°, m.p. 280—285° (decomp.) [lit., 296° (corr.)] {*Cu* salt, brown at 235°, m.p. 255° (gas) [lit., 296° (corr.)]}, which with Na–Et^{n}OH and then BzCl–NaOH gives (**VIII**). R. S. C.

2-Chloroacetylpyrrole. F. F. Blicke, J. A. Faust, J. E. Gearien, and R. J. Warzynski (*J. Amer. Chem. Soc.*, 1943, **65**, 2465—2466).—2-Chloroacetylpyrrole (**I**), m.p. 118—119° (lit., 115°), is obtained from the product of interaction of pyrrole and MgEtBr and $CH_2Cl{\cdot}CN$ in Et_2O at 0° and then the b.p. (16% yield) or from pyrrole, $CH_2Cl{\cdot}CN$, and HCl in Et_2O (20% yield). Use of MgEtI gives only 2-acetylpyrrole. NaI–$COMe_2$ converts (**I**) into 2-iodoacetylpyrrole (95%), m.p. 130—131° (lit., 81°), which with AgOAc in boiling C_6H_6 gives 2-*acetoxyacetylpyrrole* (90%), m.p. 70—71°. R. S. C.

Pyridinesulphonamide.—See B., 1944, III, 73.

Vitamin-B_6.—See B., 1944, III, 74.

Boron fluoride as a condensing agent in the Fischer indole synthesis. H. R. Snyder and C. W. Smith (*J. Amer. Chem. Soc.*, 1943, **65**, 2452—2454).—BF_3 or BF_3,Et_2O is usually approx. as effective (16 examples) as other reagents in converting hydrazones into indoles, and the products are easily isolated. In successful cases, a coloured complex is first formed which is then decomposed by heat; a solvent (AcOH) may be used. The colour indicates the following reaction mechanism: $CRMe{:}N{\cdot}NHAr \longrightarrow BF_3$ (**I**) ⇌ $CHMeR{\cdot}N{:}NAr \longrightarrow BF_3$; (**I**) → $CH_2{:}CR{\cdot}NH{\cdot}NHAr \rightarrow BF_3$ → *o*-$NH_2{\cdot}CR{:}CH{\cdot}C_6H_4{\cdot}NH_2 \rightarrow BF_3$ etc. → indole derivative. This is in line with recovery of phenylhydrazones in other forms, *e.g.*, α-keto-γ-butyrolactonephenylhydrazone, m.p. 100·5°, and *Et* α-*keto*-γ-*cyanobutyratephenylhydrazone*, m.p. 84·5°. 3-*iso*Propylindole, b.p. 138—142°/6 mm., gives a picrate, m.p. 117·5° (lit., 98—99°). Failures of the BF_3 synthesis include $CHMe{:}N{\cdot}NHPh$ and $CMe_2{:}N{\cdot}NHPh$. R. S. C.

Improved synthesis of quinaldines and 3-alkylquinolines. W. P. Utermohlen, jun. (*J. Org. Chem.*, 1943, **8**, 544—549).—A suitable oxidising agent (*O*) is obtained by running $PhNO_2$ into 20% oleum at 20—30° and then heating the mixture at 60—70° until it is completely sol. in H_2O. The following methods are used: (*A*) adding the base to a mixture of *O* and H_2O, raising the temp. to 125°, adding the aldehyde diacetate gradually, and then slowly raising the temp. to 175° while allowing H_2O and AcOH to distil; (*B*) adding the aldehyde dropwise to a mixture obtained as under (*A*) and heated at 105—110° and finally to 135° with distillation of H_2O; (*C*) Doebner–von Miller method; (*D*) adding the aldehyde dipropionate slowly to a hot, stirred mixture of As_2O_5, H_2O, base, and conc. H_2SO_4. The following -quinolines are prepared (the name of the non-basic reactant, method of prep., and % yield being placed in brackets: 2-methyl- [CHMe:CH·CHO (**I**), *B*, 43; $CHMe{:}CH{\cdot}CH(OAc)_2$ (**II**), *A*, 49·5]; 2 : 7-dimethyl- [(**II**), *A*, 47; (**I**), *B*, 62·5]; 7-chloro-2-methyl- [(**I**), *B*, 60]; 6-chloro-2-methyl- [(**II**), *A*, 55]; 2 : 6-dimethyl- $[CHMe{:}CH{\cdot}CH(O{\cdot}COEt)_2$, *A*, 49]; 6-nitro-2-methyl- [(**II**), *D*, 30]; 3-methyl-, b.p. 252—253° (picrate, m.p. 187·5°; *ethiodide*, m.p. 226·5°) $[CH_2{:}CMe{\cdot}CH(OAc)_2$ (**III**), *A*, 49; $CH_2{:}CMe{\cdot}CH(O{\cdot}COEt)_2$ (**IV**), *A*, 46; $CH_2{:}CMe{\cdot}CHO$ (**V**), *B*, 30]; 3-ethyl-, b.p. 265—266° (picrate, m.p. 199°; *ethiodide*, m.p. 215°) $[CH_2{:}CEt{\cdot}CH(OAc)_2$ (**VI**), *A*, 54; $CH_2{:}CEt{\cdot}CHO$ (**VII**), *B*, 42; (**VII**), *C*, 2·5]; 3 : 6-dimethyl-, b.p. 270—271·5°, m.p. 56·5° (picrate, m.p. 251°; *ethiodide*, m.p. 181°) [(**III**), *A*, 54]; 3 : 7-dimethyl-, b.p. 270—271·5°, m.p. 78·5° (picrate, m.p. 240·5°; *ethiodide*, m.p. 250°) [(**III**), *A*, 65; (**V**), *B*, 25]; 3 : 8-dimethyl-, b.p. 260—262° (picrate, m.p. 208·5°; *ethiodide*, m.p. 192°) [(**III**), *A*, 45]; 6-*nitro*-3-*methyl*-, m.p. 151 (picrate, m.p. 200°) [(**IV**), *D*, 35]; 7-chloro-3-methyl-, b.p. 142—144°/10 mm., m.p. 84·5° (corr.) (picrate m.p. 187·5°; *ethiodide*, m.p. 270°) [(**III**), *A*, 52]; 6-methyl-3-ethyl-, b.p. 284—285·5° (picrate, m.p. 247°; *ethiodide*, m.p. 204°) [(**VI**), *A*,

32]; 7-methyl-3-ethyl-, b.p. 282—283° (picrate, m.p. 224·5°; *ethiodide*, m.p. 180°) [(**VI**), *A*, 34; (**VII**), *B*, 35]. M.p. are corr. H. W.

5- and 7-Trifluoromethylquinolines. H. Gilman and D. Blume (*J. Amer. Chem. Soc.*, 1943, **65**, 2467—2468).—*m*-CF_3·C_6H_4·NH_2 (0·4), glycerol (1·3), As_2O_5 (0·4), and H_2SO_4 (1·1 mol.) give, after boiling, a mixture, fractionation of which yields pure 7- (**I**) (31·8%), m.p. 66—68°, b.p. 219—221°/731 mm., and *5-trifluoromethylquinoline* (5·7%), b.p. 214—215°/732 mm. (oxalate), the structure of which is proved by hydrolysis by boiling 80% H_2SO_4 to quinoline-7- and -5-carboxylic acid, m.p. 341—343° (lit., 338—340°), respectively. Li·C_6H_4Me-*p* adds normally to (**I**) in Et_2O, yielding a product which with $PhNO_2$ in Et_2O gives 2-p-*tolyl*-7-*trifluoromethylquinoline* (61%), m.p. 131—133°. R. S. C.

αβ-Diamino-ketones. I. Reactions of heterocyclic *sec.*-amines with α-bromo-β-amino-ketones. N. H. Cromwell, C. E. Harris, and D. J. Cram (*J. Amer. Chem. Soc.*, 1944, **66**, 134—137).—The following reactions conform to the mechanism previously postulated (A., 1943, II, 243). α-Bromo-β-morpholino-β-phenylethyl Me ketone (**I**) with tetrahydroquinoline (**II**) [a weaker base than morpholine (**III**)] in EtOH (51% yield) or Et_2O (20·4% yield) at room temp. gives *α-morpholino-β-tetrahydroquinolino-β-phenylethyl Me ketone*, m.p. 173°, hydrolysed by acid to PhCHO, (**II**), and morpholinoacetone (*oxime*, m.p. 104—106°). With piperidine (**IV**), which is weaker than (**III**), in EtOH, (**I**) gives an inseparable mixture of amines but the mixed product produced in Et_2O yields 10% of *β-piperidino-α-morpholino-β-phenylethyl Me ketone*, m.p. 123°. α-Bromo-β-piperidino-β-phenylethyl Me ketone with (**III**) in EtOH (32%) or Et_2O (90·2% yield) gives *α-piperidino-β-morpholino-β-phenylethyl Me ketone, forms*, m.p. 117° and 101° (hydrolysed to α-piperidinoacetone). CHPh:CBr·COPh and tetrahydro*iso*quinoline (**V**) in Et_2O–light petroleum at −10° give *α-bromo-β-tetrahydroisoquinolino-β-phenylpropiophenone* (**VI**) (85%), m.p. 117°, which with NaOEt gives (?) α-tetrahydro*iso*quinolino-β-phenylacrylophenone, an oil, but in EtOH at room temp. slowly (cf. *loc. cit.*) yields *αβ-ditetrahydro*iso*quinolino-β-phenylpropiophenone*, m.p. 184—186°, also obtained (m.p. 187°; 57% yield) from CHPhBr·CHBr·COPh by (**V**) in EtOH at 0° and then room temp. With (**III**), which is weaker than (**V**), (**VI**) in EtOH at room temp. gives *β-morpholino-α-tetrahydro*iso*quinolino-* (30%), m.p. 177° (hydrolysed to ω-tetrahydro*iso*quinolinoacetophenone), and with (**II**) (a weaker base) gives *α-tetrahydroisoquinolino-β-tetrahydroquinolino-β-phenylpropiophenone* (47%), m.p. 164°. α-Bromo-β-morpholino-β-phenylpropiophenone with (**V**) gives a mixed product, whence 13% of impure α-morpholino-β-tetrahydro*iso*quinolino-β-phenylpropiophenone, m.p. 163°, is obtained. α-Bromo-β-piperidino-β-phenylpropiophenone with (**V**), which is weaker than (**IV**), gives *α-piperidino-β-tetrahydro*iso*quinolino-* (37%), m.p. 165° (identified by hydrolysis), and with *cyclo*hexylamine, which is weaker than (**IV**), gives *α-piperidino-β-cyclohexylamino-β-phenylpropiophenone* (20%), m.p. 155°. M.p. are corr. R. S. C.

Purification of 2-nitro-5-amino-7-ethoxyacridine. A. Albert and W. Gledhill (*J.S.C.I.*, 1944, **63**, 96).—2-Nitro-7-ethoxyacridine, occurring as impurity in the prep. of the 2-nitro-5-amino-compound (**I**) (cf. A., 1942, II, 425), may be removed most suitably as its EtOH-sol. Na salt. A more conc. aq. solution of (**I**) may be obtained by dissolving in boiling H_2O containing lactic acid. F. R. S.

Transamination reaction. Effect of various nuclear substituted α-amino-α-phenylacetic acids on the course of the reaction.—See A., 1944, II, 161.

Pyrimidines. CLXXXI. Reactions characterising the oxide of 5-chloro-6-hydroxy-6-methyl-1 : 5-dic*yclo*uracil. T. B. Johnson (*J. Amer. Chem. Soc.*, 1944, **66**, 146—148; cf. A., 1943, II, 340).—The compound (**I**), $(NH<^{CO\cdot CCl}_{CO\cdot N}>CMe)_2O$, with H_2O_2 in conc. HCl at room temp. gives 5 : 5-*dichloro-6-hydroxyhydro-orotic acid* (**II**), $NH<^{CO\cdot CCl_2}_{CO\cdot NH}>C(OH)\cdot CO_2H$, m.p. 182—183° (gas), reduced by red P–HI to 5-chloro-orotic acid (**III**). With conc. HNO_3 at room temp. (**I**) gives (**III**), and with Br–H_2O at room temp. gives *5-chloro-5-bromo-6-hydroxyhydro-orotic acid*, m.p. 192—193°. $Ba(OH)_2$ converts (**II**) or (**IV**) into dialuric acid, the colour test for which is thus not sp. R. S. C.

Acid hydrolysis of a 5 : 5-dichlorohydroxy-6-arylhydrouracil. T. B. Johnson (*J. Amer. Chem. Soc.*, 1944, **66**, 148—150).—6-Phenyluracil and H_2O_2–conc. HCl give 5 : 5-*dichloro-6-hydroxy-6-phenylhydrouracil*, m.p. 209—210° (decomp.), which with red P–HI at 100° gives *5-chloro-6-phenyluracil* (**I**), m.p. 260—261°, and in hot conc. HCl gives NH.Cl and BzOH (100%) with a trace of (**I**). R. S. C.

Biological effects of benziminazole and their reversed by purines. D. W. Woolley (*J. Biol. Chem.*, 1944, **152**, 225—232).—See A., 1944, III, 435).—5-*Aminobenziminazole*, m.p. 105—106° (uncorr.), was prepared by condensing 1 : 2 : 4-$C_6H_3(NH_2)_3$ with HCO_2H. It differed (mixed m.p. depression) from the *compound*, m.p. 104—105°, obtained by reducing Bamberger and Berle's nitrobenziminazole (A., 1893, i, 435); these are therefore the 4-NH_2- and 4-NO_2-compounds.

Isatoic anhydride. I. Reactions with primary and secondary amines and with some amides. R. H. Clark and E. C. Wagner (*J. Org. Chem.*, 1944, **9**, 55—67).—Isatoic anhydride (**I**) is conveniently obtained by passing $COCl_2$ into a solution of *o*-NH_2·C_6H_4·CO_2H in dil. HCl at 50°. Strongly basic primary amines react readily with (**I**) at room temp. to 130° in most cases and some even in H_2O. Aromatic primary amines with *o*-substituents or with negative substituents in *o*- and *p*-substituents react less readily and yield largely or almost entirely " abnormal " products. The amount of CO_2 evolved in the " abnormal " reaction indicates the nearly quant. participation of (**I**). The normal change is (**I**) + NH_2R → *o*-NH_2·C_6H_4·CO·NHR (**II**) + CO_2; the " abnormal " reaction follows thus: (**I**) + (**II**) → NH_2·C_6H_4·CO·NH·C_6H_4·CO·NHR → NH_2·C_6H_4·CO·[NH·C_6H_4·CO]$_x$·NHR. In support of this mechanism it is found that no isolable normal product is obtained from equiv. amounts of (**I**) and *o*-$C_6H_4BrNH_2$ whereas some *anthranil-o-bromophenylamide*, m.p. 115·5—116·0°, is obtained if a large excees of base is used. The interaction of equiv. amounts of (**I**) and NH_2Ph is normal but when 2 equivs. of (**I**) are used the product is amorphous. When pure *o*-NH_2·C_6H_4·CO·NHPh (**III**) a (normal product) is heated with an equiv. amount of (**I**), the theoretical amount of CO_2 is evolved and the abnormal product results. Hydrolysis of the " abnormal " product from (**I**) and (**III**) by conc. HCl under pressure gives *o*-NH_2·C_6H_4·CO_2H and NH_3, the amount of the latter indicating $x = 2$. The following *anthranil-amides* are obtained: -ethyl-, m.p. 102—103° (uncorr.); -n-*propyl*-, m.p. 98·5—100°; -n-*butyl*-, m.p. 83—84°; -n-*amyl*-, m.p. 80·0—81·0°; -iso*amyl*-, m.p. 69—70°; -cyclo*hexyl*-, m.p. 155·5—156·5°; -*benzyl*-, m.p. 123·0—123·5°; -phenyl-, m.p. 125·5—126·5°; -*p*-tolyl-, m.p. 150—151·0°; -*p*-anisyl-, m.p. 125·0—126·0°; -m-*bromophenyl*-, m.p. 147·5—149°; -*p*-bromophenyl-, m.p. 148·0—149·0°; -m-*chlorophenyl*-, m.p. 130·0—131·5°; -p-*chlorophenyl*-, m.p. 140—141·5°; -2 : 4-dimethylphenyl-, m.p. 137—138° (uncorr.); -*o*-carboxyphenyl-, m.p. 205·5—206·5°; -2-*pyridyl*-, m.p. 132·0—133·0°; -4-*methyl*-2-*thiazolyl*-, m.p. 117·5—118·5°; -6-*methyl*-2-*benzthiazolyl*-, m.p. 186·0—187·0°; -*phenylimino*-, m.p. 172·0—173·0° (uncorr.); -*hydroxy*-, m.p. 78° (uncorr.); -*o*-carbethoxyphenyl-, m.p. 93·5—94·5°; -o-*carbomethoxyphenyl*-, m.p. 114·5—115·5°. M.p. are corr. unless otherwise indicated. Reaction is largely abnormal with *m*-2- and *m*-5-xylidine, *o*-NH_2·C_6H_4·CO·NH_2, *o*- and *p*-NO_2·C_6H_4·NH_2. $(CH_2$·$NH_2)_2$ and $CH_2(CH_2$·$NH_2)_2$ give the corresponding *5-dianthranoyldiamines*, m.p. 242·0—243·0° (uncorr.) and 183·0—184·0° respectively. When equiv. amounts of (**I**) and *sec.* amines are heated CO_2 is evolved but " normal " products are obtained usually in small yield if at all, the reaction products being generally resinous, gummy mixtures from which well-defined compounds cannot be isolated. If the base is kept in marked excess and conditions for rapid action are chosen moderate yields of normal products are sometimes secured. The following *anthranil-amides* are thus obtained: -*diethyl*-, b.p. 147—148°/1 mm., 158—160°/4 mm., m.p. 70—70·5° (uncorr.); -*di*-n-*propyl*-, b.p. 174—177°/4 mm. (*picrate*, m.p. 104—104·5°); -*piperidyl*-, b.p. 160—163°/1—2 mm., m.p. 73·0—74·0°; -phenylmethyl-, m.p. 127—127·5°; -*phenylethyl*-, m.p. 102·5—103°; -*phenyl*-n-*propyl*-, m.p. 75·5—76·5°. (**I**) and NH_2Ac at 180° slowly yield amorphous products, apparently mixtures. Benzoylenecarbamide with considerable amorphous material results from (**I**) and $CO(NH_2)_2$ or NH_2·CO_2Et. 3 : 4-Dihydroquinazol-4-one, m.p. 136—136·5°, and its *p*-tolyl, m.p. 144—145°, and *p*-anisyl, m.p. 194—195°, derivatives are obtained from the requisite base, (**I**), and boiling $CH(OEt)_3$. Attempts to extend the synthesis by use of $CMe(OEt)_3$ were unsuccessful. H. W.

Transformation of verdohæmochromogens into monoazahæmins. R. Lemberg (*Austral. J. Exp. Biol.*, 1943, **21**, 239—247; cf. A., 1935, 884).—A modification of the method of preparing pyridine verdohæmochromogen and verdomesohæmochromogen is described. At room temp. in presence or absence of O_2, NH_3 (but not NH_2Me) converts these compounds into monoaza-hæmin and -mesohæmin respectively. N_2H_4,H_2O in AcOH (but not conc. H_2SO_4) removes Fe from monoazahæmins, the monoazaporphyrins thus obtained being identical with Fischer's monoimidoporphyrins. The spectroscopic properties of some monoazahæmatin compounds are described and an explanation is suggested of the stability of the Fe linkage in azahæmins and its instability in verdohæmatins. W. McC.

Tetrahydrofuryl-amino-alcohols. A. Burger and G. H. Harnest (*J. Amer. Chem. Soc.*, 1943, **65**, 2382—2383).—2-Furoyl chloride and CH_2N_2–Et_2O at 0° and then room temp. give a solution of crude diazoketone, which with conc. aq. HCl gives 2-chloroacetylfuran (88%), m.p. <0°. With piperidine (2·5 mols.) in Et_2O at 0° and then room temp., this gives *2-piperidinoacetylfuran* (73%), b.p. 139—140°/4 mm., which in presence of Ni or Pt absorbs >3 mols. of H_2, but, as *hydrochloride*, m.p. 264—266° (decomp.), is reduced by boiling 3N-Al(OPr$^\beta$)$_3$–Pr$^\beta$OH to 2-α-*hydroxy-β-piperidinoethylfuran* (38%), b.p. 127—128°/5 mm. (*hydrochloride*, m.p. 172—174°).

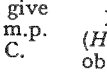
H_2–Raney Ni in EtOH at 1 atm. then yields 2-*α-hydroxy-β-piperidinoethyltetrahydrofuran* (64%), b.p. 125—126°/4 mm. (*hydrochloride*, m.p. 170—173°; *acetate hydrochloride*, m.p. 191—194°). The following are similarly prepared: 2-morpholino- (49%) (*hydrochloride*, m.p. 221—229°), and 2-*4'-methylpiperidino-acetylfuran* (51%), b.p. 133—139°/4 mm. (*hydrochloride*, m.p. 253—265°); 2-*α-hydroxy-β-morpholino-* (70%), m.p. 67—68°, b.p. 146—150°/1 mm. (*hydrochloride*, m.p. 185—186° (decomp.); *acetate hydrochloride*, m.p. 166—167° (decomp.)], and -*β*-4-*methylpiperidino-ethylfuran* (74%), m.p. 70—72°, b.p. 126—128°/4 mm. [*acetate hydrochloride*, m.p. 179—181° (decomp.)]; 2-*α-hydroxy-β-morpholino-* (41%), b.p. 138—140°/12 mm. (hygroscopic *hydrochloride*, m.p. 170—176°), and -*β*-4-*methylpiperidino-ethyltetrahydrofuran* (33%), b.p. 131—132°/4 mm. 3-Acetyl-2 : 5-dimethylfuran, paraformaldehyde, and $NHMe_2$,HCl give 3-*β-dimethylaminopropionyl*-2 : 5-*dimethylfuran hydrochloride*, m.p. 175—177°. R. S. C.

Substituted aminobenzfuranoquinolines. R. Adams, J. H. Clark, N. Kornblum, and H. Wolff (*J. Amer. Chem. Soc.*, 1944, **66**, 22—26).—Separation of benzfurano-2' : 1'-6 : 7- (**I**) from -1' : 2'-5 : 6-quinoline (**II**) is improved (cf. Mosettig *et al.*, A., 1935, 871). With HNO_3 (*d* 1·50) in 30 sec., (**I**) gives a NO_2- (84%), m.p. 267—268°, and thence (H_2–Raney Ni; EtOH; 2—3 atm.) an NH_2-derivative, m.p. 236·5—247°, which with Cl·$[CH_2]_3$·NH_2,HCl or 4-*γ*-chloro-*n*-propylmorpholine hydrochloride in $Bu^{\alpha}OH$ at 140—150° gives the *γ-diethylamino*-n-*propylamino*-, an oil, and *γ-morpholino*-n-*propylamino*-derivative, m.p. 120°, respectively. With HNO_3 (*d* 1·50), (**II**) gives NO_2-derivatives, m.p. 297—298° and 282°, reduced to NH_2-derivatives, m.p. 200° and 233°, which yield (diazo-reactions) *Br*-derivatives, m.p. 180—182° and 204°, respectively. 2-Acetamidodibenzfuran (modified prep.), m.p. 183° (lit. 178°), and HNO_3 (*d* 1·5) in AcOH give the 3-NO_2-derivative (73%), m.p. 205° (lit. 196°) (and a substance, m.p. 261—262°), hydrolysed to 3-nitro-2-aminodibenzfuran (**III**), m.p. 232—233° (lit. 222°), which with glycerol, H_3AsO_4, and H_2SO_4 at 130—140° gives 8-*nitrobenzfurano*-1' : 2'-5 : 6-*quinoline* (24%), m.p. 206—207° (cf. Kirkpatrick *et al.*, A., 1935, 985); H_2–Raney Ni + a trace of PtO_2 in EtOH at 50°/3 atm. then yields the 8-NH_2-, m.p. 197—198°, and thence, as above, the 8-*γ-morpholino*-n-*propylamino*-derivative, b.p. 238—240°/0·03 mm. 2-*Benzenesulphonamidodibenzfuran*, m.p. 162—163°, with HNO_3 (*d* 1·5) in AcOH at 18° gives the 3-NO_2-derivative (**IV**), m.p. 226—227°, hydrolysed by 25% HCl to (**III**), which with $PhSO_2Cl$ in hot C_5H_5N gives (**IV**) and the 3-*nitro*-2-*dibenzenesulphonamido*-derivative, m.p. 263—265°. H_2–PtO_2 reduces (**IV**) in EtOH at 2—3 atm. to 3-*amino*-2-*benzenesulphonamidodibenzfuran*, m.p. 227—288°, which with glycerol, $PhNO_2$, and H_2SO_4 at 145—150° gives 5-*benzenesulphonamido*- (45%), m.p. 197—198°, and thence [3 : 1 (vol.) H_2SO_4–H_2O at 145°] 5-*amino*- (**V**), m.p. 139—140°, and impure 8-*diethylamino-α-methyl*-n-*butylamino-benzfurano*-2' : 1'-5 : 6-*quinoline*, an oil. Deamination ($NaNO_2$–HCl; HPO_3) of (**V**) gives *benzfurano*-2' : 1'-5 : 6-*quinoline*, m.p. 82—83·5° (cf. *loc. cit.*). M.p. are corr. R. S. C.

5-(*p*-Aminobenzenesulphonamido)thiazole. M. H. M. Arnold and C. W. Scaife (*J.C.S.*, 1944, 103—104).—Chrysean, prepared from H.S, NaCN, with a little aq. NH_3, is 5-aminothiazole-2-thioamide (**I**), m.p. 204° (decomp.), obtained in 15—20% yield. (**I**) with $Pb(OAc)_2$ gives 5-aminothiazole-2-nitrile, which, with $CaCO_3$ followed by cautious evaporation, leads to the 2-*amide*, decomp. 156°, with dil. HCl affords the 2-*carboxylic acid*, decomp. 185°, and with PhCHO yields 5-*benzylideneaminothiazole*-2-*nitrile*, m.p. 141°. *p*-NO_2·C_6H_4·SO_2Cl and (**I**) in C_5H_5N form 5-(p-*nitrobenzenesulphonamido*)*thiazole*-2-*thioamide*, m.p. 185° (decomp.), whilst the -2-*nitrile*, m.p. 148°, and 5-(p-*acetamidobenzenesulphonamido*)*thiazole*-2-*thioamide* (**II**), m.p. 237°, and -2-*amide*, m.p. 253—255° (decomp.), are similarly prepared. Hydrolysis (NaOH–$PbCO_3$) of (**II**) gives 5-(p-*aminobenzenesulphonamido*)*thiazole*, m.p. 185° (decomp.), which is not pharmaceutically promising. F. R. S.

Reactions of nitriles as acid anammonides. E. L. Holljes and E. C. Wagner (*J. Org. Chem.*, 1944, **9**, 31—49).—Closure of the glyoxaline, oxazole, and pyrimidine rings is effected by interaction 1 : 2- or 1 : 3-$(NH_2)_2$-compounds or of *o*-NH_2·C_6H_4·OH and nitriles, the processes being essentially identical with conventional ring-closures of the Ladenburg type as effected (at lower temp.) by carboxylic acids and their anhydrides. The cases studied comprise the formation of 2-alkyl- or 2-aryl-glyoxalincs from *o*-$C_6H_4(NH_2)_2$, of 2-alkyl- or 2-aryl-benzoxazoles from *o*-NH_2·C_6H_4·OH, of 2-substituted pyrimidines from 1 : 8-$C_{10}H_6(NH_2)_2$, and of 2-substituted dihydroquinazolones from *o*-NH_2·C_6H_4·CO·NH_2. In these reactions the nitrile C is incorporated into the ring; the nitrile N is finally present as NH_4 salt or NH_3. These reactions require the presence of acid and appear to be catalysed by H. Reaction occurs slowly in absence of added acid if one of the reactants is acidic in character (*e.g.*, *o*-NH_2·C_6H_4·OH) but is markedly promoted by the presence of a strong acid which may be introduced as a salt of the NH_2-compound used. Closure of the glyoxaline and oxazole ring when HCl is used as catalyst appears to depend on the preliminary formation of the iminochloride by additive union of nitrile and acids. This reacts with an NH_2-group to yield the substituted amidine (an ammono-acyl compound), which undergoes ring-closure as do the analogous aquo-acyl compounds of the O system. The first step is relatively slow and requires the use of high temp. and extended reaction periods. The subsequent steps, each realised separately, proceed rapidly and almost quantitatively. The acid is rendered available for another cycle by the thermal dissociation of NH_4Cl, which is the by-product. 2-n-*Butyl*-, b.p. 68—70°/20 mm., and 2-n-*amyl-benzoxazole*, b.p. 114—114·5°/2 mm., appear new. H. W.

Photochemical reactions of leuco-dyes in rigid solvents. Quantum efficiency of photo-oxidation.—See A., 1944, I, 109.

Dehydrothio-*p*-toluidine. H. E. Fierz-David [with W. Brunner] (*Helv. Chim. Acta*, 1944, **27**, 1—8).—The crude primuline melt obtained from *p*-toluidine and S is separable into at least 4 components by successive use of EtOH, PhCl, and *o*-$C_6H_4Cl_2$. Distillation of it in a high vac. and without previous purification gives ~50% of pure dehydrothio-*p*-toluidine (**I**). The alcoholic extract contains also didehydrothio-*p*-toluidine, which can be sublimed unchanged at 220°/0·001 mm., but decomposes at a higher pressure and hence during the distillation of (**I**). Quant. measurements confirm the view that naphthamine-yellow *NN* (**II**) obtained by oxidising dehydrothio-*p*-toluidinesulphonic acid (**III**) with OCl′, $K_3Fe(CN)_6$, and other oxidising agents is (SO_3H·C_6H_2Me  C·C_6H_4·N)$_2$; it is most simply prepared by oxidising (**III**) to the azoxy-compound, which is then reduced to the azo-substance by Na_2S, Na_2SO_3, or glucose but not $Na_2S_2O_4$. Similarly (**I**) is quantitatively oxidised by Cl_2 in NaOH–EtOH to the unstable azoxy-compound, directly reduced to the *azo*-derivative, (C_6H_3Me  C·C_6H_4·N:)$_2$ (**III**), m.p. 322·5° (corr.), reduced by $ZnCl_2$ and HCl in EtOH to (**I**). Sulphonation of (**III**) gives an *isomeride* of (**II**) superior in shade and fastness to light; it probably contains SO_3H vicinal to N of the thiazole ring. pp′-2-*Benzthiazolylazobenzene*, m.p. 304° (corr.), is obtained by oxidation of 4-*p′*-aminophenylbenzthiazole with NaOCl and subsequent reduction with NaOCl or Na_2S, from azobenzene-1 : 4′-dicarboxylic acid and *o*-NH_2·C_6H_4·SH, and by condensation of *p*-NO_2·C_6H_4·COCl with *o*-NH_2·C_6H_4·SH and reduction of the nitrothiazole with Zn dust and NaOH. H. W.

4-Methylthiazolo(2, 3-*b*)tetrahydropyrimidine hydrobromide. F. C. Whitmore and A. W. Rytina (*J. Amer. Chem. Soc.*, 1943, **65**, 2472—2473).—2-Amino-4-methylthiazole and Br·$[CH_2]_3$·Br in boiling EtOH give 4′-*methyl*-3 : 4 : 5 : 6-*tetrahydrothiazolo*-2′ : 3′-2 : 3-*pyrimidine hydrobromide*, m.p. 235·5—237°. R. S. C.

VII.—ALKALOIDS.

Cupreine derivatives.—See B., 1944, III, 74.

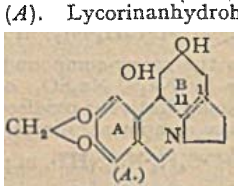
Thiocarbimides of the hydroquinine series and radical exchange with thiocarbimides and thiocarbamides. F. Zetzsche and A. Fredrich (*Ber.*, 1940, **73**, [*B*], 1420—1424).—Radical exchanges between amines or thiocarbamides and thiocarbimides are recorded. 5-*Thiocarbimidohydroquinine*, m.p. 198—200° (decomp.), is obtained from 5-aminohydroquinine and CS_2 or PhNCS in boiling C_6H_6. A similar reaction is observed with *p*-NMe_2·C_6H_4·NCS but not with CH_2:CH·CH_2·NCS or $Bu^{\beta}NCS$. 5-*Thiocarbimido-optoquin*, m.p. 196—198° (decomp.), $[\alpha]_D$ +156·3° in $CHCl_3$ (*picrate*, decomp. 150—152°), is obtained similarly. CO(NH·C_6H_4·NMe_2-*p*)$_2$, or freshly prepared *p*-NH_2·C_6H_4·NMe_2 and PhNCS at 160° afford *p*-NMe_2·C_6H_4·NCS, m.p. 65—67°. Benzidine (**I**) and boiling PhNCS yield di-4 : 4′-thiocarbimidodiphenyl, m.p. 204°, and a substance, m.p. 313—315°, which is the main product of the action of (**I**) with PhNCS in boiling COMe$_2$ or C_6H_6 or with CS(NHPh)$_2$ in boiling EtOH. (**I**) and boiling CS_2 give a material of m.p. 280—285°. H. W.

Cinchona alkaloids in pneumonia. XII. Derivatives of 6′-amino-*apo*cinchonidine. A. G. Renfrew, W. W. Carlson, and L. H. Cretcher (*J. Amer. Chem. Soc.*, 1943, **65**, 2309—2310; cf. A., 1943, II, 344).—*apo*Cupreine (**I**) (0·2 mol.) with $NaHSO_3$ (1 mol.) and NH_2·$[CH_2]_2$·OH (1·7) or NH_2·$[CH_2]_2$·NEt_2 (1·1 mols.) in H_2O at 160° give 6′-*β-hydroxy*- (30%), $[\alpha]_D$ −291° in EtOH [*dihydrochloride* (**II**)], and 6′-*β-diethylamino-ethylamino*apo*cupreine* (37%), $[\alpha]_D$ −231° in EtOH {*H camphorate*, $[\alpha]_D$ −113° in H_2O; *H* d-*tartrate* (**III**), $[\alpha]_D$ −150° in H_2O}. Bacteriostatic concns. against *Pneumococcus* II and intraperitoneal toxicities, respectively, are (**I**) 1 in 3 × 10^5, 6—8 mg., (**II**) 1 in 5 × 10^4, 6—7 mg., and (**III**) — (confluent growth at 1 in 5 × 10^4), 2 mg. per 20-g. mouse. R. S. C.

Strychnos **alkaloids. CXIII. *N*-Acetyl derivatives of *sec.*-*ψ*-strychnine and their oxidation.** H. Leuchs (*Ber.*, 1940, **73**, [*B*], 1392—1397).—Prolonged treatment of *ψ*-strychnine containing strychnine (**I**) with Ac_2O and C_5H_5N at 100° gives (**I**) and N-*acetyl-sec.-ψ-strychnine* (**II**), $C_{23}H_{24}O_4N_2$,$CHCl_3$, which does not react with NH_2·CO·NH·NH_2 and is hydrogenated (PtO_2 in AcOH) to acetyl-

dihydro-*sec.*-*ψ*-strychnine, m.p. 269° (vac.). (**II**) is oxidised by $KMnO_4$ in $COMe_2$ at 20° to the *keto-acid*, $C_{23}H_{24}O_7N_2$ (**III**), m.p. 225—230° (decomp.) after softening and darkening, $[\alpha]_D^0$ +321°/*d* in AcOH [*Me* ester, m.p. 230°, softens at 225°; *amide* (**IV**), m.p. 230—240° (decomp.), softens at 210°; *semicarbazone*, m.p. 205° (decomp.), occasionally up to 220°, becomes brown at 190°]. (**III**) scarcely absorbs H_2 (PtO_2 in AcOH) and does not give cryst. products with Na–Hg and H_2O. (**III**) is transformed by 0·5N-NaOH at 100° into a *substance*, $C_{21}H_{20}O_4N_2$ [also +1 MeOH, m.p. 280° (decomp.), softens at 260°], also obtained from (**IV**) and 13N-NH_3 at 100°. *ψ*-Brucine when similarly treated affords *N-acetyl*-sec.-*ψ*-*brucine*, which could not be obtained cryst. It is oxidised to a *keto-acid* (**V**), $C_{25}H_{28}O_9N_2$, m.p. 235—238°, softens and becomes discoloured at 225° from MeOH or m.p. 195—200° (decomp.) from H_2O, $[\alpha]_D^0$ +280°/*d* in AcOH [non-cryst. *Me* ester; *amide*, m.p. 170—188° to a resin which becomes brown at 195° and foams at 205°; *semicarbazone*, anhyd. m.p. ~215° (decomp.), darkens at 195°]. (**V**) is reduced (Na–Hg in H_2O) to the *acid*, $C_{25}H_{30}O_8N_2$, m.p. 235—237° (slight decomp.), softens at 225°, and is converted by 0·5N-NaOH at 100° into the *compound*, $C_{23}H_{24}O_6N_2$, m.p. 229—231° (vac.), softens at 225°. H. W.

Lycoris **alkaloids. XVII. Constitution of lycorine.** H. Kondo and H. Katsura (*Ber.*, 1940, **73**, [*B*], 1424—1430).—Lycorine (**I**) is (*A*). Lycorinanhydrohydromethine (**II**), m.p. 71—71·5°, obtained



(*A*.)

by the Emde degradation of the α(*β*)-methochloride of (**I**), yields CH_2O but not MeCHO when ozonised in $CHCl_3$. Catalytic hydrogenation (PtO_2 in AcOH) of (**II**) yields the H_6-derivative, m.p. 70—72° (*picrate*, m.p. 218—221°). Oxidation ($KMnO_4$ at 30°) of (**II**) leads to hydrastic acid. An unusual addition of H to nucleus B therefore occurs during the Emde degradation. (**II**) is converted into the *methiodide*, m.p. 235°, and thence into the methochloride, which is reduced (Na–Hg–H_2O) to the *compound*, $C_{18}H_{21}O_2N$, b.p. 165° (bath)/0·01 mm. (*picrate*, m.p. 147—148°), which gives a *methiodide*, m.p. 186—187°, and thence a methochloride, reduced to *de*-N-*anhydrohydrolycorine*, b.p. 160—170° (bath)/0·03 mm. Reduction (Na–Hg) of the lycorinanhydromethine obtained by the Hofmann degradation gives a product not identical with (**II**). Reduction (Na–Hg) of lycorinanhydromethine methochloride (corresponding *methiodide*, decomp. 226°) leads to (**II**). Spectrographic curves of (**I**), dihydrolycorine, and the two Ac derivatives are closely similar, showing that the double linking in the B nucleus of (**I**) is not conjugated with that of the nucleus and lies between $C_{(11)}$ and The curve of (**II**) is completely different, showing that in it the double linking $C_{(11)}$–$C_{(1)}$ has been hydrogenated and that the remaining double linking is conjugated with that of nucleus A. H. W.

Delphinium **alkaloids. II. Ajacine.** J. A. Goodson (*J.C.S.*, 1944, 108—109).—Ajacine, $C_{34}H_{46}O_9N_2.2H_2O$, m.p. 154°, $[\alpha]_D^{22}$ +49·5° in EtOH, is acetylanthranoyl-lycoctonine; since on hydrolysis with NaOH–EtOH it gives *o*-NHAc·C_6H_4·CO_2H and lycoctonine, and with 10% HCl affords AcOH and anthranoyl-lycoctonine. F. R. S.

VIII.—ORGANO-METALLIC COMPOUNDS.

Aliphatic arsonic acids. VI. Attempted preparation of diarsonosuccinic acid and its salts. A. R. Marquez (*Rev. Fac. Cienc. Quím., La Plata*, 1942, **17**, 109—116).—$(CHBr{\cdot}CO_2Et)_2$ with As_2O_3 in NaOH yields a solution, which with $BaCl_2$ gives *Ba*$_2$ *aa'-diarsonosuccinate* (*Ca*$_2$ and *Na*$_4$ *salts*). F. R. G.

Relations between chemical activity and absorption in the ultra-violet of organic molecules. V. Interaction of atoxyl with the halogen derivatives of substituted amides of malonic acid. K. G. Naik, R. K. Trivedi, and C. M. Mehta (*J. Indian Chem. Soc.*, 1943, **20**, 372—373).—$CHBr(CO{\cdot}NHAr)_2$ but not $CCl_2(CO{\cdot}NHAr)_2$ react with atoxyl in boiling aq. EtOH to give p-*arsonoanilinomalondi*-p-*bromoanilide*, m.p. 251—253° (decomp.), -p-*toluidide*, m.p. 233° (decomp.), and -*benzylamide*, m.p. 266° (decomp.). H. M. C.

Mercurials from aliphatic glycols. A. J. Shukis and R. C. Tallman (*Amer. Chem. Soc.*, 1943, **65**, 2365—2366).—R·(O·$[CH_2]_3$)$_n$·OH (R = H or alkyl) with C_2H_4 and $Hg(OAc)_2$ at 70—90° and then aq. NaCl gives OEt·$[CH_2]_2$·HgCl, m.p. 92°, *compounds*, Et·(O·$[CH_2]_2$)$_x$·O·$[CH_2]_2$·HgCl in which x = 1, m.p. 34—35° (lit., an oil), 2, m.p. 50° (lit., an oil), 3, m.p. 53—54°, and 4, an oil, *Hg β-β'-β''-hydroxyethoxyethoxyethyl chloride*, m.p. 70—72°, and *Hg β-β'-hydroxyethoxyethyl chloride*, m.p. 88—89°. OH·$[CH_2]_2$·Cl gives similarly *Hg β-β'-chloroethoxyethyl chloride*, m.p. 54°. The appropriate glycols yield *compounds*, OH·$[CH_2]_n$·O·$[CH_2]_2$·HgCl, in which n = 3, m.p. 114—116°, 4, m.p. 92—93°, and 6, m.p. 98—99°. OH·CH_2·CHMe·OH gives a *compound*, m.p. 80—81°. OH·$CH(CH_2{\cdot}OH)_2$ gives a *compound*, m.p. 88—91°. Distribution coeffs. (solubility in C_6H_6/solubility in H_2O) and bacteriostatic activity against *Staph. aureus* are recorded for the products; close parallelism exists. R. S. C.

Mercuri derivatives.—See B., 1944, III, 75.

IX.—PROTEINS.

Conversion of globular into oriented fibrous proteins. I. By heat and mechanical working. F. R. Senti, C. R. Eddy, and G. C. Nutting (*J. Amer. Chem. Soc.*, 1943, **65**, 2473).—Heating casein, *β*-lactoglobulin (**I**), hæmoglobin, ovalbumin (**II**), edestin, zein, or proteins from peanuts or soya beans in H_2O and then stretching or extruding them in hot or cold H_2O or H_2O vapour gives products having *β*-keratin structure (*X*-ray). *X*-Ray spacings are quoted for (**I**) and (**II**). The tensile strength of protein fibres, thus treated, is greatly increased. R. S. C.

***o*-Benzoic sulphinide ferridehæmoglobin. Reaction of hæmoglobin with nitrite. Verdohæmochromogens.**—See A., 1944, III, 323.

X.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

American musk. II. Scent glands of the beaver. P. G. Stevens (*J. Amer. Chem. Soc.*, 1943, **65**, 2471; cf. A., 1942, II, 178).—The neutral products (6·3 g.) obtained by boiling 10% KOH–EtOH from the Et_2O-extract of dried beaver-glands (113 g.) yield an oily, unsaturated *substance*, $C_{11}H_{18}O_2$, b.p. 147—155°/1 mm., having a spicy odour. The neutral products from another sample of glands yielded a mixture containing a similar liquid and a small amount of cholesterol. The acidic products include BzOH, *p*-anisic, and amorphous castoric acids. Large-ring ketones and fatty acids are absent. R. S. C.

Lignin and related compounds. LXXV. Alkaline nitrobenzene oxidation of plant materials and application to taxonomic classification. R. H. J. Creighton, R. D. Gibbs, and H. Hibbert. **LXXVI. Alkaline nitrobenzene oxidation of maize stalks. Isolation of *p*-hydroxybenzaldehyde.** R. H. J. Creighton and H. Hibbert. **LXXVII. Re-investigation of the ethanolysis products of maple wood.** M. Kulka, H. E. Fisher, S. B. Baker, and H. Hibbert. **LXXVIII. Chromic acid oxidation of lignin-type substances, wood ethanolysis products, and wood.** W. S. MacGregor, T. H. Evans, and H. Hibbert (*J. Amer. Chem. Soc.*, 1944, **66**, 32—37, 37—38, 39—41, 41—44; cf. A., 1944, II, 162).—LXXV. Alkaline $PhNO_2$-oxidation of 47 woods, almost all gymnosperms, yields only vanillin (**I**) (15—24% calc. on Klason lignin) and of angiosperms yields generally a 1 : 3 mixture (35—51%) of (**I**) and syringaldehyde (**II**). Certain primitive angiosperms yield a 1 : 1 mixture of (**I**) and (**II**). Gnetales genera yield (**I**) and (**II**) and may thus be angiosperms. Very few Coniferales yield both (**I**) and (**II**). Behaviour on oxidation parallels that in the Maule reaction and may be used for taxonomic classification

LXXVI. Maize-stalk meal with $PhNO_2$–aq. NaOH at 160° yields 4·5, 2·6, and 1·4% of pure (**I**), (**II**), and *p*-OH·C_6H_4·CHO (**III**), respectively. OMe-contents of *m*-nitrobenzoylhydrazides indicate the possibility of existence of (**III**) also in maize cobs, bamboo and rye straw; presence of (**III**) may distinguish mono- from di-cotyledons.

LXXVII. The alkali-sol. part of the H_2O-sol. ethanolysis of maple wood lignin yields, by improved methods (cf. A., 1939, II, 172), 3·1% of 4 : 3 : 1-OH·C_6H_3(OMe)·CO·CHMe·OEt and 3·2% of 4 : 3 : 5 : 1-OH·C_6H_2(OMe)$_2$·CO·CHMe·OEt, m.p. 73—74° (lit. an oil), and a mixture yielding a 1 : 3 mixture of the respective derived Me ethers. Pure compounds isolated by ethanolysis of maple wood amount to 9·8% of the Klason lignin, but the actual contents are considered to be much higher.

LXXXVIII. CrO_3-oxidation of compounds containing Ar–C_3 gives 0·9—0·95 mol. of AcOH (reduced somewhat if the Ar is very stable) if the C_3 includes a terminal Me, but only traces of AcOH if terminal Me is present. Spruce or maple wood gives traces of AcOH. Extracted amorphous maple EtOH-lignin gives very little AcOH, but that from spruce gives 1 AcOH per 4—5 Ar–C_3 units; more AcOH is obtained if the spruce lignin is subjected again to HCl–EtOH. Support is thus given to the view that native lignin contains no terminal Me and that its presence in products from wood is due to rearrangement of products of hydroxyconiferyl alcohol type. R. S. C.

Lignin. XLII. Vanillincarboxylic acid and related acids.—See A., 1944, II, 161.

Pigments of cottonseed.—See A., 1944, III, 444.

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A II—Organic Chemistry.

JULY, 1944.

I.—ALIPHATIC.

Chemical behaviour of free ethyl at low temperatures. G. Semerano L. Riccoboni, and F. Callegari (*Ber.*, 1941, **74**, [*B*], 1297—1308).—When $AgNO_3$ (1 mol.) and $PbEt_4$ (1·5—1·6 mols.) interact in EtOH at −80°, some decomp. of AgEt occurs; when this is completed by warming, the gas evolved contains C_nH_6 (53·2), C_4H_{10} (36·2), C_4H_4 (9·9%), and traces of CO_2 and CO. The Et thus yields only C_4H_{10} and $C_2H_6 + C_2H_4$. The deficiency of C_2H_4 is accounted for by interaction thereof with EtOH to yield Et_2O (isolated; cf. C., 1944, Part 3); in MeOH MeOEt is probably similarly formed. The reaction mechanism is discussed. R. S. C.

Manufacture of ethylene.—See B., 1944, II, 125.

Physical data of Δ^{α}-olefines and n-paraffins. A. W. Schmidt, V. Schoeller, and K. Eberlein (*Ber.*, 1941, **74**, [*B*], 1313—1324).—M.p., b.p., d, n, and η are recorded for most of the Δ^{α}-olefines and paraffins containing 5—30 C, including the following: Δ^{α}-C_nH_{2n} in which $n = 9$ m.p. −88°, b.p. 33·5°/11 mm., 10 m.p. −66·3°, b.p. 52°/11 mm., 11 m.p. −49·5°, b.p. 74·8°/11 mm., 12 m.p. −33·6°, b.p. 89—89·5°/11 mm., 13 m.p. −22·2°, b.p. 104°/11 mm., 15 m.p. −4°, b.p. 135·2°/11 mm., 17 m.p. 11°, b.p. 157°/11 mm., and 21 m.p. 35·5°, b.p. 134°/0·04 mm.; n-C_nH_{2n+2} in which $n = 8$ m.p. −57·0°, b.p. 124°/11 mm., 11 m.p. −24·8°, b.p. 74°/11 mm., 13 m.p. −5·5°, b.p. 104°/11 mm., 17 m.p. 21·2°, b.p. 157°/11 mm., 21 m.p. 39·4°, b.p. 129°/0·05 mm., 26 m.p. 56·4°, b.p. 169°/0·05 mm., and 30 m.p. 65·5°, b.p. 202°/0·05 mm. The olefines are prepared from MgRHal and $CH_2{:}CH{\cdot}CH_2Br$ in Et_2O. n-Octane was prepared by the Wurtz–Fittig reaction (60% yield), n-C_nH_{2n+2} (n = 11—21) by hydrogenation of C_nH_{2n}, and n-$C_{26}H_{54}$ and -$C_{30}H_{62}$ by electrolysis of the K salt in EtOH. R. S. C.

Structure of copolymers of *iso*butylene and isoprene. J. Rehner, jun. (*Ind. Eng. Chem.*, 1944, **36**, 46—51).—O_3 degradation, in $CHCl_3$ or, better, in CCl_4, applied to investigation of the structure of *iso*butylene–isoprene copolymers of various degrees of unsaturation, indicates that the isoprene units are exclusively in the $\alpha\delta$-position as in natural rubber; any units with $\alpha\beta$- or $\gamma\delta$-addition must be $\ll$1% of the isoprene present. No occurrence of the C_5H_8 units in sequences could be detected, and the C_5H_8 must enter the growing chain in a random manner. D. F. T.

Separation of divinylacetylene and ethinylbutadiene ($\Delta^{\alpha\varepsilon}$-hexadien-$\Delta^{\gamma}$- and $\Delta^{\gamma\varepsilon}$-hexadien-$\Delta^{\alpha}$-inene).—See B., 1944, II, 126.

Effect of natural inhibitors on the photochemical oxidation of iodoform. K. Weber and M. Czirfusz (*Ber.*, 1941, **74**, [*B*], 1338—1342).—Light-petroleum extracts of oatmeal or cornflour decrease the rate of autoxidation of CHI_3 in light. This is shown not to be due to absorption of the effective light. R. S. C.

Allylic rearrangements. XIV. Hydrolysis of butenyl chlorides.—See A., 1944, I, 157.

Polyene series. XII. Ethynylcarbinols from sorbaldehyde and octatrienal. Poly-carbon anionotropic rearrangements. I. M. Heilbron, E. R. H. Jones, and J. T. McCombie. **XIII. Acetylenyl glycols from polyene aldehydes and their rearrangement with acids.** I. M. Heilbron, E. R. H. Jones, and R. A. Raphael. **XIV. Anionotropic rearrangements of carbinols from condensation of crotonaldehyde with vinyl- and β-methylvinyl-acetylene.** I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon. **XV. Condensation of carbonyl compounds with propenylethynylcarbinol and hex-3-en-5-yn-2-ol.** J. Cymerman, I. M. Heilbron, A. W. Johnson, and E. R. H. Jones. **XVI. Condensation of αβ-unsaturated ketones with 1-hexyne.** J. Cymerman, I. M. Heilbron, and E. R. H. Jones (*J.C.S.*, 1944, 134—136, 136—139, 140—141, 141—144, 144—147; cf. A., 1943, II, 249).—XII. Sorbaldehyde (I) in liquid NH_3 with C_2HNa gives *octa-δζ-dien-α-yn-γ-ol* (II), b.p. 71—74°/0·5 mm. Octatrienal (III) (similar conditions) gives *deca-δζθ-trien-α-yn-γ-ol* (IV), b.p. 94—96°/1 mm., m.p. 73·5—74·5°. (II) undergoes anionotropic rearrangement with H_2SO_4 (N_2 atm.) to give *octa-γε-dien-α-yn-η-ol*, b.p. 62—63°/0·5 mm., unstable in air, which on hydrogenation (PtO_2) and oxidation (CrO_3) yields $COMe{\cdot}C_6H_{13}$-n. Similarly (IV) gives *deca-γεη-trien-α-yn-ι-ol*, m.p. 82—83°, which affords $COMe{\cdot}C_8H_{17}$-n. Replacement of an ethenoid by an acetylenic linking has a negligible effect on the location of the absorption max.

XIII. (I) ($C{\cdot}MgBr$)$_2$ (from C_2H_2 and MgEtBr) in N_2 followed by aq. NH_4NO_3 gives *tetradeca-ββδκμ-tetraen-η-yne-ζι-diol* (V), m.p. 95—102°. (III) (similar conditions) gives *octadeca-ββδζμξπ-hexaen-ι-yne-θλ-diol* (VI), m.p. 154°. (V) undergoes anionotropic rearrangement (aq. H_2SO_4, N_2 atm.) to *tetradeca-γεμλ-tetraen-η-yne-βν-diol* (VII), m.p. 115—116° (sealed tube). Similarly (VI) gives *octadeca-γεηλνο-hexaen-ι-yne-βρ-diol* (VIII), sinters 145°, m.p. 149° (sealed tube). (VII) on hydrogenation and oxidation (NaOBr) yields $[CH_2]_{10}(CO_2H)_2$. (VIII) on hydrogenation gives *octadecane-βρ-diol*, which is oxidised to $[CH_2]_{14}(CO_2H)_2$. (VII) and (VIII) resemble corresponding polyenes in their light-absorption properties.

XIV. Mg vinylacetylenyl bromide with $CHMe{:}CH{\cdot}CHO$ (IX) gives *octa-βη-dien-ε-yn-δ-ol* (X), b.p. 72—73°/3·5 mm. (*α-naphthylurethane*, m.p. 95—96°), also given by (IX) and $CH_2{:}CH{\cdot}C{:}CH$ with Na in liquid NH_3. (X) with H_2SO_4 (N_2) is isomerised to *octa-γη-dien-ε-yn-β-ol* (XI), b.p. 78°/4 mm. Hydrogenation and subsequent oxidation of (XI) yields $COMe{\cdot}C_6H_{13}$-n. Methylvinylacetylene and (IX) (similar conditions) give *η-methylocta-βη-dien-ε-yn-δ-ol* (XII), b.p. 62—68°/3 mm. (*α-naphthylurethane*, m.p. 99°), which isomerises to *η-methylocta-γη-dien-ε-yn-β-ol* (XIII), b.p. 75—78°/2 mm., 27° (bath)/10^{-4} mm. (*α-naphthylurethane*, m.p. 89°). (XIII) is hydrogenated to η-methyloctan-β-ol, b.p. 57°/3 mm. (*α-naphthylurethane*, m.p. 75°), which gives (CrO_3) η-methyloctan-β-one, b.p. 78°/17 mm. (semicarbazone, m.p. 132—133°). Absorption spectra of (X), (XI), (XII), and (XIII) are analogous in location and intensity of max. to each other and compounds previously described.

XV. $CHMe{:}CH{\cdot}CH(OH){\cdot}C{:}CH$ condenses (Grignard method) with $COPh_2$, $Pr^{\alpha}CHO$, PhCHO, and (IX) respectively to *αα*-diphenylhept-ε-en-β-yne-αδ-diol, m.p. 131°, *dec-β-en-ε-yne-δη-diol* (XIV), b.p. 52° (bath)/10^{-4} mm. [two *bisphenylurethanes*, m.p. 125° and 153° (decomp.); *bis-α-naphthylurethane*, m.p. 194° (decomp.)], α-phenylhept-ε-en-β-yne-αδ-diol, b.p. 80—90° (bath)/10^{-4} mm., m.p. 108°, and deca-βθ-dien-ε-yne-δη-diol (XV), b.p. 90—100° (bath)/10^{-4} mm., m.p. 91°. Hex-γ-en-ε-yn-β-ol (XVI) with $Pr^{\alpha}CHO$, PhCHO, *p*-$OMe{\cdot}C_6H_4{\cdot}CHO$, COMeEt, (IX), and $COPh_2$ respectively yields *dec-γ-en-ε-yne-βη-diol* (XVII), b.p. 72° (bath)/10^{-4} mm., *α-phenylhept-δ-en-β-yne-αζ-diol*, b.p. 78° (bath)/10^{-4} mm., *α-(p-anisyl)hept-δ-en-β-yne-αζ-diol*, b.p. 78° (bath)/10^{-4} mm., m.p. 19—20°, *γ-methylnon-ζ-en-δ-yne-γθ-diol*, b.p. 63° (bath)/10^{-4} mm., *deca-γθ-dien-ε-yne-βη-diol* (XVIII), b.p. 75° (bath)/10^{-4} mm., and *αα-diphenylhept-δ-en-β-yne-αζ-diol* (XIX), b.p. 85° (bath)/10^{-4} mm. Both (XV) and (XVIII) give deca-γη-dien-ε-yne-βι-diol, b.p. 110—115° (bath)/10^{-4} mm., and (XIV) with aq. H_2SO_4 yields (XVII). The products from (XVI), with the exception of (XIX) which dissociates into $COPh_2$, exhibit light-absorption characteristics consistent with the conjugated vinylacetylene chromophore in their mol.

XVI. $CBu^{\alpha}{:}CH$ (converted into $CBu^{\alpha}{:}C{\cdot}MgBr$ by MgEtBr) condenses with $COMe{\cdot}CH{:}CH_2$, $COMe{\cdot}CH{:}CHMe$, mesityl oxide (XX), and oct-γ-yn-β-one respectively to give at room temp. *γ-methylnon-α-en-δ-yn-γ-ol* (XXI), b.p. 61—61·5°/3·5 mm., *δ-methyldec-β-en-ε-yn-δ-ol* (XXII), b.p. 62—62·5°/2 mm., *ββ-dimethyldec-β-en-ε-yn-δ-ol* (XXIII), b.p. 69—69·5°/3 mm., and η-methyltrideca-εθ-diyn-η-ol. (XXI), (XXII), and (XXIII) show no light absorption. With aq. H_2SO_4, (XXI) gives *γ-methylnon-β-en-ο-yn-α-ol* (XXIV), b.p. 75·5—76°/3·5 mm. (*α-naphthylurethane*, m.p. 69—70°). (XXIV) yields H_2–PtO_2) γ-methylnonan-α-ol, b.p. 121°/24 mm. (*α-naphthylurethane*, m.p. 49°), which gives (CrO_3) β-*n*-hexylbutyric acid (*p-toluidide*, m.p. 76—77°). (XXII) similarly gives *ο-methyldec-γ-en-ε-yn-β-ol* (XXV), b.p. 84°/2 mm., 28° (bath)/10^{-4} mm. (*α-naphthylurethane*, m.p. 71°); δ-methyldecan-β-ol, b.p. 104°/12 mm. (*α-naphthylurethane*, m.p. 63°), and δ-methyldecan-β-one, whilst (XXIII) yields *ββδ-dimethyl-γ-en-ε-yn-β-ol* (XXVI), b.p. 35° (bath)/10^{-4} mm. (XVI) condenses with (XX) to give *ββδ-deca-βη-dien-ε-yne-δι-diol*, b.p. 60° (bath)/10^{-4} mm., which undergoes some rearrangement with aq. H_2SO_4. The anionotropic rearrangements above are easier than those for related *sec.* carbinols; it is suggested that this is due to the inductive effect of the *tert.* Me group which facilitates the separation of the hydroxylic anion. The isomerisation products (XXIV), (XXV), and (XXVI) exhibit light-absorption characteristic of the vinylacetylene chromophore. D. G.

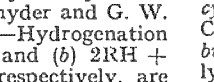
βγδε-Di*iso*propylidene-*DL*-xylitol. R. M. Hann, A. T. Ness, and C. S. Hudson (*J. Amer. Chem. Soc.*, 1944, **66**, 73—76).—βγδε-Di*iso*propylidene-*DL*-xylitol (modified prep.; cf. Tipson *et al.*, A., 1943,

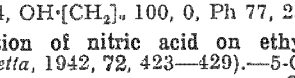
II, 149), m.p. 33—34° (*α-acetate*, m.p. 45—46°; *α-benzoate*, m.p. 61—62°), gives an *α-p*-toluenesulphonate (**I**), m.p. 77—78° (*loc. cit.*, 70—71°), which with NaI in $(CH_2Ac)_2$ at 60° gives the *α-iodide*, m.p. 57—59°, reduced by H_2–Raney Ni in Ba(OMe)$_2$–MeOH at 27°/810 mm. to *α-deoxy-βγδε-diisopropylidene*-DL-*xylitol* (**II**), b.p. 88—90°/6—7 mm. (**II**) consumes 3 HIO_4 in H_2O at 25°. Boiling 20% AcOH hydrolyses (**II**) to *α-deoxy*-DL-*xylitol*, a syrup, which reduces 2·87 $NaIO_4$ in H_2O at 25°, giving 0·91 MeCHO. These facts prove the structure of (**I**). *αβγδ*-Dibenzylidene-*D*-sorbitol *εζ*-di-*p*-toluenesulphonate with NaI in $COMe_2$ at 100° gives 2 *p*-$C_6H_4Me{\cdot}SO_3Na$ and *αβγδ-dibenzylidene*-D-*sorbitoleën*, m.p. 187—188°, $[\alpha]_D^{20}$ +19·0° in $CHCl_3$, reduced by H_2–Raney Ni to *αβγδ-dibenzylidene-εζ-deoxy*-D-*sorbitol*, m.p. 184—185°, $[\alpha]_D^{20}$ +39·4° in $CHCl_3$, whence it appears that *p*-$C_6H_4Me{\cdot}SO_2$ esterified to contiguous primary and *sec.* OH are both removed by NaI (cf. *loc. cit.*).
R. S. C.

Isomerisation of trialkyl phosphites. G. M. Kosolapov (*J. Amer. Chem. Soc.*, 1944, **66**, 109—111).—Interaction of Et_3PO_3 with Bu^aBr (at 150°), *n*-$C_6H_{13}Br$ (at 133° and 150°), or $(CH_2Br)_2$ (at 150°) is followed by measuring the rate of evolution of EtBr. According to the proportions of the reactants, $(CH_2Br)_2$ reacts according to the equation, $2Et_3PO_3 + (CH_2Br)_2 \rightarrow 2EtBr + CH_2[PO(OEt)_2]_2$, or $Et_3PO_3 + (CH_2Br)_2 \rightarrow EtBr + (OEt)_2PO{\cdot}[CH_2]_2{\cdot}Br$ (**I**). (**I**) is, however, not isolated because of its instability. An induction period occurs in all the reactions, during which $PRBr(OEt)_3$ accumulates; this is shortened by rise in temp.
R. S. C.

Purification of ethers.—See B., 1944, II, 126.

Sulphur linkage in vulcanised rubbers. Reaction of methyl iodide with sulphur compounds.—See B., 1944, II, 187.

Carbon–carbon cleavage in the hydrogenolysis by Raney nickel catalyst of ethylenedithiol and its ethers. H. R. Snyder and G. W. Cannon (*J. Amer. Chem. Soc.*, 1944, **66**, 155—156).—Hydrogenation (Raney Ni) of $(CH_2{\cdot}SR)_2$ gives (*a*) $2RH + C_2H_6$ and (*b*) $2RH + 2CH_4$. The following yields of C_2H_6 and CH_4, respectively, are recorded: R = $[CH_2]_3{\cdot}CH(NH_2){\cdot}CO_2H$ 66, 34,  56, 44, $OH{\cdot}[CH_2]_3$ 100, 0, Ph 77, 23, and H 86, 14%.
R. S. C.

Action of nitric acid on ethyl *iso*dehydracetate. L. Panizzi (*Gazzetta*, 1942, **72**, 423—429).—5-Carbethoxy-4 : 6-dimethylcumalin (Et *iso*dehydracetate),  , with HNO_3 (*d* 1·52) gives its 3-NO_2-derivative (**I**) (cf. Angeli, A., 1893, i, 197), reduced by $SnCl_2$–HCl–Et_2O to the stannichloride of 3-*amino-5-carbethoxy-4 : 6-dimethylcumalin*, m.p. 80—81° (*Bz* derivative, m.p. 128—129°), which with conc. aq. NH_3 gives a *product*, $C_{10}H_{15}O_5N$, m.p. 203—205° (decomp.), regarded as $CO_2Et{\cdot}CHAc{\cdot}CMe{:}C(NH_2){\cdot}CO_2H$ or $CO_2Et{\cdot}CHAc{\cdot}CHMe{\cdot}C(:NH){\cdot}CO_2H$. With $NHPh{\cdot}NH_2$–AcOH at the b.p., (**I**) gives Et 1-phenyl-3 : 5-dimethylpyrazole-4-carboxylate, CO_2, and $MeNO_2$.
E. W. W.

Esterification under the catalytic influence of acid chlorides. K. Freudenberg and W. Jakob (*Ber* 1941, **74**, [*B*], 1001—1002).—Small amounts of AcCl, $ClCO_2Et$, $SOCl_2$, or *n*-$C_{17}H_{35}{\cdot}COCl$ cause very rapid esterification of acids with alcohols at $\gg 20°$. Examples are the Me and Et esters of veratric, *p*-nitrobenzoic, and stearic acid. Polyacrylic acid is thus 40% esterified; $OH{\cdot}CHPh{\cdot}CO_2Me$ is not thus formed. A mol. compound of the acid chloride with probably, the acid is formed, which reacts faster with the alcohol than with H_2O; thus, ethylene glycol monopalmitate is formed only if an excess of glycol is present and the dipalmitate cannot be obtained. The method is preferable to that using HCl.
R. S. C.

Chemical morphology of liquids. III. Liquid-crystalline aliphatic monocarboxylic acids. C. Weygand, R. Gabler, and J. Hoffmann (*Z. physikal. Chem.*, 1941, **B**, **50**, 124—127).—$\Delta^{\alpha\gamma}$-Nonadienoic acid, prepared by condensation of $CHBu^a{:}CH{\cdot}CHO$ with $CH_2(CO_2H)_2$ followed by decarboxylation, passes above 23° into a characteristic nematic phase, becoming clear at 49°. The melt may be supercooled to ~10°, and still lower with small drops, but no smectic phase appears. It is suggested that the diene group adjacent to the CO_2H plays the same rôle as the C_6H_6 ring in the mesomorphic *p-n*-alkylbenzoic acids, conferring rigidity on a considerable length of the dimeric acid mol., and that such rigidity, provided that the m.p. is sufficiently low, will result in mesomorphic properties. The mesomorphic states of the many *p*-derivatives of C_6H_6, of sterol derivatives, and of Tl and alkali-metal soaps are discussed in the light of this concept.
W. R. A.

Shellac. XIII. Transformation of aleuritic into hexadecenoic acid. W. Nagel and W. Mertens (*Ber.*, 1941, **74**, [*B*], 976—982).—Me *iso*propylidenealeuritate, an oil, prepared from Me aleuritate, $COMe_2$, and a little H_2SO_4 at room temp., with *p*-$C_6H_4Me{\cdot}SO_2Cl$–C_5H_5N at room temp. gives the oily *o-p*-toluenesulphonate (**I**), which with NaOMe–MeOH at 70—75° yields *aleuritic acid o-Me ether* [*θι-dihydroxy-o-methoxypalmitic acid*] (80%), m.p. 76° (*Me* ester, m.p. 65°). With NaI in $COMe_2$ at ~70°, (**I**) gives the *o*-I-ester, which with Zn and H_2SO_4 and then boiling 3N-KOH gives *θι*-dihydroxypalmitic acid (**II**), m.p. 89—90°. The Me ester thereof with *p*-$C_6H_4Me{\cdot}SO_2Cl$–C_5H_5N gives an oily ester, converted by NaI–$COMe_2$ and then Zn dust in AcOH into *Me* Δ^{θ}-n-*hexadecenoate*, b.p. 181—183°/15 mm. Δ^{θ}-n-*Hexadecenoic acid* (**III**), m.p. 33°, obtained therefrom by 2N-KOH, gives a dibromide, m.p. ~30°, and is converted by $KMnO_4$–KOH into (**II**) (~40%). Ag_2O oxidises (**II**) (0·6) in boiling C_6H_6 to azelaic (0·25) and heptoic acid (0·03 g.). (**III**) is accompanied by an isomeric oily acid, oxidised by $KMnO_4$ to a $(OH)_2$-acid, m.p. 125°. (**III**) may be identical with hypogaic acid.
R. S. C.

Unsaturated synthetic glycerides. III. Unsaturated symmetrical mixed diglycerides. B. F. Daubert and H. E. Longenecker (*J. Amer. Chem. Soc.*, 1944, **66**, 53—55).—Glyceryl *α*-esters and CPh_3Cl in quinoline at 100° give *glyceryl α-CPh$_3$ ether α′-dodecoate* (**I**), m.p. 47·0°, *α′-tetradecoate*, m.p. 56·0°, *α′*-palmitate, m.p. 62·0°, and *α′*-stearate, m.p. 66·0°, converted by oleyl chloride in quinoline–$CHCl_3$ at room temp. into the *β-oleates*. Hydrolysis of these products by HCl in light petroleum at ~5° involves migration, yielding *glyceryl α-n-dodecoate*, m.p. 32·0°, *α-n-tetradecoate*, m.p. 41·0°, *α*-palmitate, m.p. 46·0°, and *α*-stearate, m.p. 54·0°, *α′-oleate*, structures of which are proved by hydrogenation. *Glyceryl α-n-dodecoate α′-stearate*, m.p. 62·0°, is also obtained from (**I**) by way of *glyceryl α-CPh$_3$ ether β-n-dodecoate α′-stearate*, m.p. 25·0°.
R. S. C.

Long-chain acids containing a quaternary carbon atom. III. W. H. Hook and (Sir) R. Robinson (*J.C.S.*, 1944, 152—154; cf. A., 1944, II, 17).—Et *α*-methylhexylidenecyanoacetate (**I**) treated with *n*-$C_5H_{11}{\cdot}MgBr$ in presence of Cu_2I_2 gives *Et α-cyano-ββ-di-n-amylbutyrate* (**II**), b.p. 137—139°/0·3 mm., and *Et α-cyano-β-methyloctoate*, b.p. 90—92°/0·1 mm. (**II**), after boiling with H_2SO_4–AcOH–H_2O, and decarboxylation (160°/vac.), yields *ββ-di-n-amylbutyric* [*β-methyl-β-n-amyloctoic*] *acid*, b.p. 125—130°/0·3 mm. *Et α-methyldecylidenecyanoacetate*, b.p. 146—148°/0·25 mm. (from $COMe{\cdot}C_9H_{19}$-*n* and $CN{\cdot}CH_2{\cdot}CO_2Et$), with $MgBu^aBr$ and Cu_2I_2 gives *Et α-cyano-β-n-butyl-β-n-nonylbutyrate*, b.p. 150—160°/0·2 mm., which on hydrolysis and decarboxylation gives *β-n-butyl-β-n-nonylbutyronitrile* (**III**), b.p. 130—136°/0·3 mm., and a little *β-methyldodecoamide*, m.p. 87°. (**III**) after hydrolysis and treatment with MeOH and H_2SO_4 yields *Me β-n-butyl-β-n-nonylbutyrate* (**IV**), b.p. 116—120°/0·1 mm. The hydrolysis also gives *β-n-butyl-β-n-nonylbutyramide*, b.p. 165—180°/0·45 mm., which yields (**IV**) on hydrolysis. Alkaline hydrolysis of (**IV**) gives *β-n-butyl-β-n-nonylbutyric acid*, b.p. 155—157°/0·3 mm. (**I**) with *n*-$C_7H_{15}{\cdot}MgBr$ yields *Et α-cyano-β-n-amyl-β-n-heptylbutyrate*, b.p. 155—158°/0·12 mm., which affords *β-n-amyl-β-n-heptylbutyronitrile*, b.p. 123—126°/0·25 mm., *Me β-n-amyl-β-n-heptylbutyrate*, b.p. 115—117°/0·2 mm., and *β-n-amyl-β-n-heptylbutyric acid*, b.p. 144—149°/0·45 mm. Similarly *Et α-methyloctylidenecyanoacetate*, b.p. 165—168°/13 mm., with *n*-$C_7H_{15}{\cdot}MgBr$ gives *Et α-cyano-ββ-di-n-heptylbutyrate*, b.p. 168—172°/0·5 mm., *ββ-di-n-heptylbutyronitrile*, b.p. 145—150°/0·5 mm., *Me ββ-di-n-heptylbutyrate*, b.p. 135—140°/0·4 mm., and *ββ-di-n-heptylbutyric acid*, b.p. 168—172°/0·6 mm. *Et α-n-propylisohexylidenecyanoacetate*, b.p. 120—125°/0·4 mm. (from $COPr^a{\cdot}C_5H_{11}$-*iso*), with $CH_2Bu^{\beta}{\cdot}MgI$ gives *Et α-cyano-β-n-propyl-ββ-diisoamylpropionate*, b.p. 140—145°/0·7 mm., *β-n-propyl-ββ-diisoamylpropionitrile*, b.p. 115—118°/0·8 mm., *Me β-n-propyl-ββ-diisoamylpropionate*, b.p. 100—108°/0·3 mm., and *β-n-propyl-ββ-diisoamylpropionic acid*, b.p. 138—145°/0·3 mm. (*amide*, m.p. 52—53°). Of the above, the C_{16} acids are most active bactericidally, but not more so than diheptylacetic acid. The prep. of *θ-keto-ζ-methyl-ζ-n-amyltridecane*, b.p. 165—170°/19 mm., is also described.
D. G.

Linear superpolyesters from dilinoleic acid. J. C. Cowan and D. H. Wheeler (*J. Amer. Chem. Soc.*, 1944, **66**, 84—88).—Superpolymers (*i.e.*, mol. wt. >10,000) are obtained by heating dilinoleic acid (**I**) with $OH{\cdot}[CH_2]_{10}{\cdot}OH$, and hydrogenated dilinoleyl glycols. Owing to loss of $(CH_2{\cdot}OH)_2$, this glycol gives superpolymers only by glycolysis in presence of *p*-$C_6H_4Me{\cdot}SO_3H$. Superpolymers from (**I**) are essentially similar to those from hydrogenated (**I**), so that the unsaturation plays no vital rôle. They are sol. in $CHCl_3$ and are converted into cross-linked, non-cryst. solids by long exposure to air or by heating at 290—300°. Determination of mol. wt. by end-group assay or η gives concordant results, except at very high mol. wts. when end-group assay has a large experimental error.
R. S. C.

Chemistry of *Phytomonas tumefaciens*. II. Composition of acetone-soluble fat. S. F. Velick and R. J. Anderson. **III. Phytomonic acid, a new branched-chain fatty acid.** S. F. Velick (*J. Biol. Chem.*, 1944, **152**, 523—531, 533—538).—II. *P. tumefaciens* (**I**), grown on a medium in which sucrose is the main source of C, contains 6·4% of lipins and 41·7% of $COMe_2$-sol. fat, m.p. 9°. The latter contains ~70% of free fatty acids, which after hydrolysis with boiling KOH–EtOH (N_2) afford palmitic acid (**II**), and (mainly) liquid acids which are reduced (H_2–PtO_2), esterified (CH_2N_2), and hydrolysed to stearic acid (**III**) + some (**II**), and a little of an *acid* (**IV**), $C_{20}H_{40}O_2$, m.p. ~15° (liquid Me ester). The presence of glycerol in the H_2O-sol. constituents after hydrolysis suggests that the fat is a mixture of free fatty acids and neutral glycerides. In the unsaponifiable fraction, some Ph_2O, m.p. 28° (Br_2-derivative,

m.p. 55·6—56°), is isolable, but is not found in organisms grown under slightly different conditions.

III. The hydrolysis product (boiling 5% aq. H_2SO_4 under N_2) of the phosphatide from (I) is reduced (H_2–PtO_2–EtOH), (II) + (III) are removed, and a branched-chain acid, " *phytomonic acid*," m.p. 24° (*hydrazide*, m.p. 56·6°), identical with (IV), is isolated through its Me ester. It is probably a homologue of tuberculostearic acid.

A. T. P.

Use of potassium *tert*-amyloxide for the alkylation of acetoacetic ester and its alkyl substitution products. W. B. Renfrow, jun. (*J. Amer. Chem. Soc.*, 1944, **66**, 144—146).—KO·CMe_2Et–CMe_2Et·OH is approx. as efficient as NaOEt–EtOH for condensation of *n*-AlkBr (Alk = Et or Bu) with $CH_2Ac·CO_2Et$, but is superior for branched-chain AlkBr (Alk = Pr^{β} 50%, Bu^{β} 61%, *iso*-C_5H_{11} 72% yield), and much superior for alkylation of $CHRAc·CO_2Et$ ($CEt_2Ac·CO_2Et$ 75%, $CBu^{a}_2Ac·CO_2Et$ 70% yield). Superiority of KO·CMe_2Et is due to the stronger base hindering the reverse Claisen equilibrium and depressing dissociation of the enolates.

R. S. C.

Acidity and diazomethane reaction of *C*-methylacetoacetic ester. F. Arndt, L. Loewe, and B. Beyer (*Ber.*, 1941, **74**, [*B*], 1460—1464).—The rate of reaction of $COR·CH_2·CO_2Et$ with CH_2N_2 depends on the amount of enol in the equilibrium mixture, which parallels the acidity of the enol. The inductive effect of R is the primary factor. When *O*-methylation is slow, formation of the γ-ethylene oxide (and thence the *C*-Me derivative) occurs. $CHMeAc·CO_2Et$ (I) reacts very slowly with CH_2N_2 in Et_2O, but in Et_2O–MeOH gives, more quickly, a mixture of (II), estimated by its OMe content to contain 1 part of $OMe·CMe{:}CMe·CO_2Et$ and 4 parts of *Et βγ-epoxy-αβ-dimethyl*-n-*butyrate* (III). Treating (II) with conc. aq. HCl–Et_2O at −20° (2 hr.) and then room temp. (1 hr.) gives *Et β-hydroxy-α-methyl-β-chloromethyl*-n-*butyrate* (IV), b.p. 98—100°/8 mm., which with 2·5% aq. KOH–Et_2O gives pure (III), b.p. 62—63°/5 mm., whence Ac_2O and a little $FeCl_3$ at room temp. and then 100° give *Et β-acetoxy-α-methyl-β-acetoxymethyl*-n-*butyrate* (V), b.p. 88—91°/2 mm. (III) and (IV), but not (V), give abnormally high OMe vals. (I) gives a less acid enol than does $CH_2Ac·CO_2Et$ (VI). When the Na derivative of (VI) is treated with MeI in PhMe, unchanged (VI) is removed from the product in Et_2O by aq. NH_3 and the (I) is then extracted by N-NaOH at 0° and immediately recovered therefrom by cold 10% H_2SO_4 under Et_2O; the Et_2O residue contains a little $CMe_2Ac·CO_2Et$. The yield of (I) depends largely on the loss in alkali. Pure (I) has b.p. 59°/5 mm.

R. S. C.

***r*-α-Hydroxy-ββ-dimethyl-γ-butyrolactone (pantolactone).** J. H. Ford (*J. Amer. Chem. Soc.*, 1944, **66**, 20—21).—$OH·CH_2·CMe_2·CHO$ (? its dimeride, *4-hydroxy-5 : 5-dimethyl-2-β-hydroxy*-tert.-*butyl*-1 : 3-*dioxan*), m.p. 78—81°, with NaCN and then HCl in aq. $CaCl_2$, finally at 100°, gives a solid solution, m.p. 89·8—91·0°, b.p. 117—121°/10 mm., α 0, of the *d*- and *l*-forms of pantolactone.

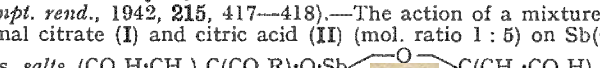
R. S. C.

Branched-chain fatty acids. II. Synthesis in the C_{19}- and C_{25}-series. Preparation of keto-esters. J. Cason and F. S. Prout (*J. Amer. Chem. Soc.*, 1944, **66**, 46—50; cf. A., 1942, II, 297).—$CH_2Bu^{\beta}·MgBr$ and $CdCl_2$ in Et_2O–N_2 at 0° and then room temp. give $Cd(CH_2Bu^{\beta})_2$, which with $CO_2Me·[CH_2]_2·COCl$ (I) in C_6H_6 exothermally and then at the b.p. gives $CH_2Bu^{\beta}·CO·[CH_2]_2·CO_2Me$ (73·5%; 42·5% obtained in Et_2O), b.p. 116·5—117°/8 mm., and a little $CO_2Me·[CH_2]_4·CO_2Et$. $Cd(CH_2Bu^{\beta})_2$ and ground $(CH_2·CO)_2O$ in boiling C_6H_6 give $CH_2Bu^{\beta}·CO·[CH_2]_2·CO_2H$ (30·8%), b.p. 152—153°/4 mm., and fractions, b.p. 100—111°/4 mm. and 147—150°/4 mm. $Cd(CH_2Bu^{\beta})_2$ and $CO_2Et·[CH_2]_8·COCl$ give similarly *Et ι-keto-ν-methyl*-n-*tetradecoate* (85%), b.p. 180—182°/3 mm. $CdMe_2$ gives similarly $COMe·[CH_2]_4·CO_2Et$ (II) (86·5%) [semicarbazone, m.p. 104·8—107° (lit. 107°)] and $COMe·[CH_2]_8·CO_2Et$ (III) (89·6%) (*semicarbazone*, m.p. 110·7—112·8°). Hydrolysis of crude (I) yields the derived acid, dimorphic, m.p. 59° (immediate), partly resolidifies, remelts at 60° (cf. lit.), $[CH_2]_8(CO_2H)_2$ (IV), and *dodecane-βλ-dione*, m.p. 67·4—67·8° [obtained by further interaction of (III) with $CdMe_2$]. $Zn(CHMePr^{a})_2$ and (I) in Et_2O at −5° to −7° give *γ-keto-δ-methyl*-n-*octoate* (21·5%), b.p. 130·5—130·7°/21 mm. $Cd(CH_2·CHMeEt)_2$ and (I) in Et_2O give 24—27% of crude $CHMeEt·CH_2·CO·[CH_2]_2·CO_2Me$, b.p. 132—134°/16 mm., which by hydrolysis yields the derived acid [*semicarbazone*, m.p. 137—138° (decomp.)] and by Zn–Hg in aq. HCl gives $CHMeEt·[CH_2]_4·CO_2H$, b.p. 98—105°/1—2 mm. (*amide*, m.p. 90·4—91·6°). $COMe·[CH_2]_4·CO_2Et$ and MgEtI in Et_2O–N_2 give an alcohol, which by I at 180—190° and then H_2–PtO_2 in EtOH yields $CHMeEt·[CH_2]_4·CO_2Et$ (V), b.p. 125·5—127·5°/36 mm. Na–EtOH reduces (V) to $CHMeEt·[CH_2]_5·OH$, b.p. 108—111°/22 mm., which with anhyd. HBr gives the bromide, b.p. 105—108°/21 mm. Similar reactions yield *Et ι-keto-ο-methyl*-n-*octadecoate* (VI) (76·5%), b.p. 192—195°/2 mm., and a fraction, b.p. 130°/2 mm., whence hydrolysis yields (IV) and n-*hexadecane-γξ-dione*, an oil. Hydrolysis of (VI) yields the derived *acid*, m.p. −54·1°, and Clemmensen reduction gives *Et ο-methyl*-n-*octadecoate* (78·6%), b.p. 170—175°/1·5 mm., hydrolysed to the derived *acid* (VII), m.p. 49·9—50·6° (*amide*, m.p. 92·5—93°; *tribromoanilide*, m.p. 106·2—106·9°). Attempts to prepare (VII) starting from $CHMeEt·CH_2·OH$ yielded the less sol. $Pr^{\beta}·[CH_2]_{15}·CO_2H$ owing to the presence of $CHMePr^{a}·OH$ as impurity. n-$C_{18}H_{37}·MgBr$ and (II) in Et_2O at 0° and then the b.p. give a OH-ester (VIII) (and a little $C_{36}H_{74}$), which with I at 180—190° and then PtO_2–H_2–EtOH yields *Et ε-methyl*-n-*tetracosoate* (29·2%), b.p. 211—214°/~0·5 mm., and thence the derived acid, m.p. 57·5—60·5° (*amide*, m.p. 83·9—85·3°; *tribromoanilide*, m.p. 94·4—97·2°). Hydrolysis of (VIII) by KOH–EtOH gives *ε-hydroxy-ε-methyl*-n-*tetracosoic acid*, m.p. 46—47·3°. Similar methods lead to *Et ι-methyl*-n-*tetracosoate*, b.p. 218—222°/~0·5 mm., and the derived *acid*, m.p. 50·5—51·5° (amide, m.p. 77·5—78·5°; *tribromoanilide*, m.p. 84·2—84·8°). M.p. are corr.

R. S. C.

Kinetics of transformation of 2-ketopolyhydroxy-acids.—See A., 1944, I, 157.

Alkali antimonyl citrates. Y. Volmar and G. Geottelmann (*Compt. rend.*, 1942, **215**, 417—418).—The action of a mixture of a normal citrate (I) and citric acid (II) (mol. ratio 1 : 5) on $Sb(OH)_3$ gives *salts* $(CO_2H·CH_2)_2C(CO_2R)·O·Sb<^{O}_{O·CO}>C(CH_2·CO_2H)_2,H_2O$ in which R = K, Na, or NH_4. With a mixture of (I) and (II) in equimol. ratio the *product* is



(R = K, Na, or NH_4). A dialkali salt could not be obtained. The antimonyl citrates are very stable, very sol. in H_2O to acid solutions, and very sparingly sol. in org. media. They can be heated with H_2O at 110° without undergoing hydrolysis; Sb is not immediately pptd. from them by H_2S. Mineral acids and alkalis decompose them with formation of $Sb(OH)_3$. They are very sensitive to ultra-violet light, Sb being liberated.

H. W.

β-Acetyl-δε-*iso*propylideneascorbic acid. C. S. Vestling and M. C. Rebstock (*J. Biol. Chem.*, 1944, **152**, 585—591).—Acetylation of δε-*iso*propylideneascorbic acid, m.p. 221·6° (decomp.), $[\alpha]_D^{28·5}$ +22° in H_2O, by a rapid stream of keten in anhyd. $COMe_2$ at room temp. is followed by indophenol titration. The resulting *β-acetyl-δγ-iso*propylideneascorbic acid (I), m.p. 115—116°, $[\alpha]_D^{27}$ +27·4° in MeOH, does not react readily with CH_2N_2 in MeOH at −40° or in dioxan at 13°. Hydrolysis of (I) in 3% HPO_3 at 70° and pH 1·9 indicates a pseudo-first-order reaction. A linear rate of decomp. of (I) is noted during 2 hr., equiv. to 0·1% per min. Hydrolysis is ~75% in 1 hr., and during the 2nd hr. oxidative decomp. occurs at such a rate as to make it impossible to obtain accurate vals.

A. T. P.

Raman spectra of vitamin-*C* and its oxidation products.—See A., 1944, I, 142.

Preparation of *d*-galacturonic acid and *l*-galactonic acid and derivatives thereof.—See B., 1944, II, 128.

Plant growth substances. XXXIII. Constitution of biotin from egg-yolk. F. Kogl, J. H. Verbeek, H. Erxleben, and W. A. J. Borg (*Z. physiol. Chem.*, 1943, **279**, 121—139).—In relationship to the sulphohexoic acid (I) obtained from biotin, the degradation of β-sulphohexoic acid (II) by alkali fusion is studied. Δ^{α}-*n*-Hexenoic acid, prepared from Et α-bromohexoate and quinoline at 185° and subsequent hydrolysis of the unsaturated ester, adds NH_4HSO_3 to form the NH_4 salt of (II) (*m-toluidine* salt, m.p. 145°). With 50% KOH at 170° the SO_2 is removed. The product is hydrogenated (PtO_2), heated at 200°, and again hydrogenated. The *n*-hexoic acid produced is identified as *p*-phenylphenacyl ester, m.p. 72°. (I) with KOH at 225° (lower temp. does not remove SO_2) and subsequent hydrogenation affords $CHMePr^{\beta}·CO_2H$, identified as the *p*-phenylphenacyl ester, m.p. 73°. The γ-sulpho-acid was synthesised by the following stages. $CH_2Ph·SNa + CH_2Br·CH{:}CH_2$ gives *CH_2Ph allyl sulphide* (III), b.p. 110—155°/13 mm. Addition of HBr to (III) affords *β-bromo-α-benzylthiolpropane* (IV), b.p. 98·5—99°/0·05 mm. With $CHNa(CO_2Et)_2$ (IV) gives *Et α-carbethoxy-γ-benzylthiol-β-methyl*-n-*butyrate* (V), b.p. 147°/0·007 mm., converted by way of the Na compound of (V) with MeI into *Et α-carbethoxy-γ-benzylthiol-αβ-dimethyl*-n-*butyrate* (VI), b.p. 136°/0·003 mm. [also obtainable from (III) and $CHMe(CO_2Et)_2$]. Hydrolysis of (VI) gives the free *acid* (VII), m.p. 120°, decarboxylated to *γ-benzylthiol-αβ-dimethyl*-n-*butyric acid* (VIII). Fission of (VIII) with Na in NH_3 affords γ-thiol-αβ-dimethyl-*n*-butyric acid, an oil, the Ba salt of which is oxidised by Br to *Ba γ-sulpho-αβ-dimethyl*-n-*butyrate* (IX) (*m*-toluidine salt, m.p. 103—105°). The *anhydride* of (IX), b.p. (bath)/0·02—0·03 mm., forms an *aniline* salt of the anilide, m.p. 168°. SO_2 is not removed from (IX) by alkali fusion below 270°; (IX) is therefore excluded as a possibility for (I). $CHPr^{\beta}(CO_2H)_2$, $NHMe_2$, and CH_2O afford *dimethylaminomethylisopropylmalonic acid*, m.p. 112·5°, which when boiled in slightly acid solution gives *α-methylene-β-methylbutyric acid* (X), b.p. 98°/18 mm. (*p-phenylphenacyl* ester, m.p. 76—77°). With AcSH (X) yields as an oil, later cryst., the *acetylthiol* compound (XI), b.p. 120—123°/0·65 mm., which with 10% aq. NaOH gives *β-methyl-α-thiolmethyl*-n-*butyric acid* (XII), b.p. 92—94°/0·7 mm., m.p. 40°. With Br–$BaCO_3$ (XII) affords *β-methyl-α-sulphomethyl*-n-*butyric acid* (XIII) (*m-toluidine* salt, m.p. 153—154°), which with 50% KOH loses SO_2 only at 225—230°. (XI) is resolved by means of cinchonidine, the salt fraction cryst. from $COMe_2$ having $[\alpha]_D$ −78·9° in EtOH; the acid is an oil, $[\alpha]_D$ −4·17° in $CHCl_3$. It is converted as above into

optically active (**XIII**), with no measurable rotation. The *m*-toluidine salt, m.p. 156°, gives no m.p. depression with the corresponding product from (**I**). When heated with $SOCl_2$ in C_6H_6, (**XIII**) gives the *anhydride* (**XIV**), b.p. 113°/0·02 mm. (**XIV**) with NH_2Ph in C_6H_6 affords the *aniline* salt of the *anilide* (**XV**), m.p. 223° (micro), 248° (ordinary method, quick heating). The corresponding optically active *component* has m.p. 234—235° (micro), 250—251° (ordinary). With CH_2N_2, (**XV**) or the free anilide yields the *Me* ester (**XVI**), m.p. 134°, of the anilide. The optically active Me ester has m.p. 135°, $[\alpha]$ +2·12° in $COMe_2$. By similar treatment (**I**) gives the anilide aniline salt [cf. (**XIV**)], m.p. 224—225°, and the Me ester [cf. (**XV**)], m.p. 135°, and the respective mixed m.p. showed no depression. The constitution $\begin{matrix}NH\cdot CH(CO_2H)\cdot CH\cdot S\cdot CH_2\\ |\\ CO\cdot NH\text{————}CH\text{—}CHPr^{\beta}\end{matrix}$ is assigned to biotin from egg yolk (now termed α-biotin). J. H. B.

Decomposition of chloral hydrate by piperidine. L. Yang and P. F. Hu (*J. Chinese Chem. Soc.*, 1943, **10**, 190—193).—$CCl_3\cdot CH(OH)_2$ (**I**) is decomposed by piperidine (**II**) at 25°; with (**II**) in excess, the reaction is unimol., but with equal concn. of (**I**) and (**II**) or with excess of (**I**), reaction is bimol. It is probable that with excess of (**II**), the formation of the adduct, (**I**) + (**II**), is instantaneous, and the reaction rate represents mainly the decomp. of the adduct. In excess of (**I**), addition is slower than decomp. A. T. P.

Reaction of acetaldehyde with ethyl bromide at 400°.—See A., 1944, I, 157.

Derivatives of aldol and crotonaldehyde. III. Constitution of paraldol. E. Spath and H. Schmid (*Ber.*, 1941, **74**, [*B*], 859—866).—Removing volatile ingredients at 100°/10 mm. from commercial aldol, keeping the residue at 18°, and then treating with Et_2O gives paraldol (**I**), m.p. ~95—97° (decomp.; vac.), which at the b.p., 125° (bath)/15 mm., regenerates aldol, whence (**I**) is rapidly re-formed on keeping. With Ac_2O–C_5H_5N at 18° or, better, keten in boiling Et_2O, (**I**) gives its diacetate (**II**), b.p. 120—125° (bath)/1 mm. With H_2–Pd-black in warm AcOH, (**II**) gives 4-methyl-2-*β*-acetoxy-*n*-propyl-1 : 3-dioxan, b.p. 80—85° (bath)/1 mm. (and AcOH), hydrolysed by 3% NaOH–MeOH at room temp. to *4-methyl-2-β-hydroxy-n-propyl-1 : 3-dioxan*, m.p. −62° to −59°, b.p. 90° (bath)/8 mm., which is also obtained from aldol, $OH\cdot CHMe\cdot[CH_2]_2\cdot OH$, and HCl at 50° (proof of structure). 0·05N-HCl–EtOH–H_2O at 70·0° hydrolyses 1 Ac of (**II**) in ~4 min., but the second Ac only very slowly, 0·58 OAc surviving after 85 min. With NH_2OH–MeOH at 18° (**II**) gives a 1 : 1 mixture of aldoxime and acetylaldoxime. (**I**) is, therefore, considered to be *4-hydroxy-6-methyl-2-β-hydroxy-n-propyl-1 : 3-dioxan*; the OAc which is readily removed from (**II**) is the semi-acetal group at $C_{(4)}$. R. S. C.

Higher primary alkylamines and their reaction with carbon disulphide. T. Wagner-Jauregg, H. Arnold, and H. Rauen (*Ber.*, 1941, **74**, [*B*], 1372—1378).—Higher NH_2Alk are not obtained from AlkHal by liquid NH_3 but are prepared by *o*-$C_6H_4(CO)_2NK$ (**I**), followed by N_2H_4. With CS_2 in cold EtOH they give 70—75% of amine dithiocarbamates, but after prolonged boiling give excellent yields of thiocarbamides, by means of which they can be characterised. Turpin's method (A., 1888, 1174) gives only thiocarbamides. Use of $Hg(OAc)_2$ and CS_2 in boiling EtOH gives the alkylthiocarbimides. Thus are obtained cryst. cetylamine, oleylamine (from oleyl bromide, b.p. 180—200°/0·15 mm.), cryst., b.p. ~175°/0·2 mm. (*hydrochloride*, m.p. 161—165°; *cinnamoyl* derivative, m.p. 77—78·5°), hydnocarpylamine, chaulmoogrylamine, cryst., b.p. 185°/0·1 mm., *cetylamine* N-*cetyldithiocarbamate*, m.p. 100—101°, s-*dicetyl-*, m.p. 88—89°, s-*dioleyl-*, m.p. 67—69°, and s-*dihydnocarpylthiocarbamide*, m.p. 65—66°, *cetyl-*, cryst., b.p. 180—194°/0·35 mm., and *oleyl-thiocarbimide*, b.p. 200—210°/0·4 mm., N-*oleyl-*, m.p. 72—75°, b.p. 260—270°/0·4 mm., *N*-hydnocarpyl-, m.p. 57°, and *N*-chaulmoogryl-phthalimide, cryst. R. S. C.

Preparation of unsymmetrical secondary aliphatic amines. K. N. Campbell, A. H. Sommers, and (Miss) B. K. Campbell (*J. Amer. Chem. Soc.*, 1944, **66**, 82—84).—Adding RCHO gradually to NH_2R' and KOH at 0° gives 52—83% of NPr^{α}:CHMe, b.p. 74—81°, *ethylidene-butylamine*, b.p. 98—106°, NEt:CHEt, b.p. 70—76°, *propylidene-n-butylamine*, b.p. 118—127°, n-*butylidene-ethylamine*, b.p. 100—108°, -n-, b.p. 120—124°, and -iso-*propylamine*, b.p. 100—111°, and -cyclo*hexylamine*, b.p. 78—88°/20 mm., NPr^{α}:$CHPr^{\beta}$, b.p. 108—114°, iso*amylidene-n-propylamine*, b.p. 130—139°, and -n-*butylamine*, b.p. 90—96°/100 mm. Hydrogenation (PtO_2 or, more slowly, Pd–C) of the aldimines in EtOH at 2—3 atm. gives 33—63% of $NHEtPr^{\alpha}$, b.p. 77—80°/738 mm. (α-naphthylthiocarbamide, m.p. 122—123°; *hydrochloride*, m.p. 223—224°), $NHEtBu^{\alpha}$, b.p. 109°/737 mm. (α-naphthylthiocarbamide, m.p. 125°; *hydrochloride*, m.p. 197°), $NHPr^{\alpha}Bu^{\alpha}$, b.p. 92—93°/200 mm. [α-naphthylthiocarbamide, m.p. 136—137°; *hydrochloride*, m.p. 267—268° (decomp.)], $NHPr^{\alpha}Bu^{\beta}$, b.p. 83—84°/200 mm. [α-naphthylthiocarbamide, m.p. 143—144°; *hydrochloride*, m.p. 278—282° (decomp.)], $NHPr^{\alpha}\cdot C_5H_{11}$-*iso*, b.p. 106—107°/200 mm. [α-naphthylthiocarbamide, m.p. 137—138°; *hydrochloride*, m.p. 264—265° (decomp.)], $NHPr^{\beta}Bu^{\alpha}$, b.p. 121°/733 mm. (α-naphthylthiocarbamide, m.p. 91·5—92·5°; *hydrochloride*, m.p. 195—196°), $NHBu^{\alpha}\cdot C_5H_{11}$-*iso*, b.p. 64—65°/14 mm. (α-naphthylthiocarbamide, m.p. 117·5—118·5°; *hydrochloride*, decomp. 290°), and *cyclo*hexyl-*n*-hexylamine, b.p. 87—90°/12 mm. [α-naphthylthiocarbamide, m.p. 107—108°; *hydrochloride*, m.p. 278—283° (decomp.)]. Reduction occurs in presence of Raney Ni, but yields no *sec.* amine. R. S. C.

Availability of ε-acetyl-*l*-lysine and ε-methyl-*dl*-lysine for growth.—See A., 1944, III, 490.

Invert soaps. IX. Azinium salts. O. Westphal (*Ber.*, 1941, **74**, [*B*], 1365—1372).—$NRR'\cdot NH_2$, in which R is a short-chain and R' a long-chain alkyl, react with MeHal or EtHal to give $NH_2\cdot NMeRR'$}Hal (*A*) etc. MeI and EtI react exothermally; EtBr reacts best in EtOH during several hr.; EtCl reacts only in EtOH at 100° and causes some substitution to give inseparable mixtures. Addition of Alk_2SO_4 or $CH_2Br\cdot CO_2Alk$ is quant. *A* are sparingly sol. in H_2O; supersaturated solutions may form gels. *A* are surface-active and ppt. proteins. Against lactic acid bacteria they are approx. as effective as are NR_4X, max. effectiveness occurring at R' = octyl. $NR_2\cdot NHR'$ are also approx. as effective, but the max. occurs at $R' = C_{12}H_{25}$. Against staphylococci also *A* are about as effective as NR_4X or $NR_2\cdot NHR'$, but the max. occurs at $R' = C_{12}H_{25}$. $NRR'\cdot NH\cdot CO\cdot CH{:}CH\cdot CO_2H$ is effective in acid, but not in alkaline, solution. $NR_2\cdot NHR'$ are prepared by interaction of $NR_2\cdot NH_2$ with AlkCl. The following are described: NNN-*tri-n-hexylhydrazinium chloride* (prep. from $C_6H_{13}Cl$ and N_2H_4 in EtOH at 150°), m.p. 65°; N-*methyl*-N-n-*dodecylhydrazine hydrochloride*, m.p. 70—72°; N-*methyl*-N-*ethyl*-N-n-*dodecyl-*, m.p. 82°, and *-cetylhydrazinium bromide*, m.p. 94°; NN-*dimethyl*-N-n-*dodecyl-*, m.p. 96°, and *-cetyl-hydrazinium iodide*, m.p. 163—164·5° (decomp.) (corresponding *methosulphate*, m.p. 99—100°); *N*-methyl-*N*-*n*-dodecyl-*N*-allylhydrazinium chloride and bromide, oils; N-*cyano*-N-*methyl*-N-n-*dodecylhydrazinium bromide*, m.p. 71—72°; *N*-methyl-*N*-cetylhydrazine, m.p. ~36°, b.p. 173°/3 mm.; N-*methyl*-N-*carbethoxymethyl*-N-*cetylhydrazinium bromide*, m.p. 68—69°; NN-*diethyl*-N'-n-*cetyl-*, b.p. 107—109°/13 mm., and -N'-n-*dodecyl-hydrazine*, b.p. 172—174°/11 mm. *n*-$C_{12}H_{25}\cdot MgCl$ and $NEt_2\cdot CH_2\cdot CN$ in Et_2O give, after hydrolysis, diethyltridecylamine, b.p. 169°/12 mm. (*hydrochloride*, m.p. 77—79°). $C_{12}H_{25}\cdot NMe\cdot NH_2$ and $(CH\cdot CO)_2O$ in boiling C_6H_6 give *H* N-*malein*-N'-*methyl*-N'-n-*dodecylhydrazide*, m.p. 69·5—70·5°. M.p. are m.p. (micro). R. S. C.

αζ-Diamino-βγ-δε-dimethylenemannitol. W. N. Haworth, R. L. Heath, and L. F. Wiggins (*J.C.S.*, 1944, 155—157).—Mannitol with fuming HCl (sealed tube at 95°) gives αζ-dichloromannitol (**I**), m.p. 174°, and other compounds not yet investigated. (**I**) condenses with CH_2O to *αζ-dichlorodimethylenemannitol* (**II**), m.p. 156°, with a little of an *isomeride*, m.p. 96°, $[\alpha]_D$ −18·2°. (**II**) is also obtained by treating (**I**) with paraformaldehyde and H_2SO_4. (**II**), fused with *o*-$C_6H_4(CO)_2NK$ in presence of glycerol, gives (20% yield) *αζ-diphthalimidodimethylenemannitol* (**III**), m.p. 277°, hydrolysed (hydrazine method) to *αζ-diaminodimethylenemannitol monohydrate* (**IV**), m.p. 48—52°, $[\alpha]_D^{18}$ +67·7° in $CHCl_3$. (**II**) with NH_3 in MeOH (autoclave at 150°), followed by aq. $Ba(OH)_2$ (N_2), yields 60% of (**IV**). (**IV**) gives *αζ-diaminodimethylenemannitol dihydrochloride* (**V**), m.p. 220—224° (decomp.), reconverted into (**IV**) by aq. $Ba(OH)_2$. Crystallising (**IV**) from dry EtOAc–Et_2O yields the anhyd. *diamine* (hygroscopic), m.p. 50°. (**IV**) gives *αζ-bis-N-salicylideneaminodimethylenemannitol*, m.p. 191—192°, *αζ-bis*-p-*benzenesulphonamidodimethylenemannitol*, m.p. 249—251°, and several salts: *oxalate*, m.p. 280° (decomp.), *adipate* (**VI**), m.p. 205°, *sebacate* (**VII**), m.p. 162°, *dimethylene*-l-*idosaccharate*, decomp. 270—300°. (**VI**) and (**VII**) when heated above their m.p. give polymers which do not give oriented fibres when cold-drawn. With *o*-$C_6H_4(CO)_2O$ (**IV**) gives (**III**), and with $CH_2Ac\cdot CO_2Et$ a *compound*, $C_{20}H_{32}O_8N_2$, m.p. 120°, $[\alpha]_D^0$ +67·2° in $CHCl_3$ (structure suggested). Hydrolysis of (**V**) (10% HCl) gives *αζ-diaminomannitol dihydrochloride*, m.p. 238—240° (decomp. 302—305°). (**II**), with KOH in EtOH, or fused with Na, yields di(methylenedioxy)-$\Delta^{\alpha\varepsilon}$-hexadiene, m.p. 80°, $[\alpha]_D^0$ +281·5° in $CHCl_3$. This reaction supports the suggestion that the $\cdot CH_2\cdot$ groups bridge Cβ–Cδ and Cγ–Cε. D. G.

Degradation of amino-acids in the animal organism. I. *l*-Alanine.—See A., 1944, III, 426.

Action of amino-acids on α-ketohexonates. K. Maurer and K. Knoevenagel (*Ber.*, 1941, **74**, [*B*], 1003—1006).—Me α-ketogluconate with $NH_2\cdot CHMe\cdot CO_2Et$ or $NH_2\cdot CH_2\cdot CO_2Et$ in MeOH in absence of air gives the NH_2-ester salt, and thence by KOH the K salt (33 and 41%, respectively), of *iso*ascorbic acid. Similar reactions occur with (i) $NH_2\cdot[CH_2]_2\cdot CO_2Et$ or arginine, and (ii) Me or Et α-ketogulonate. The primary products could not be crystallised. The reaction could not be followed by changes in α or by I-titration; yields thus recorded average 60—100%. R. S. C.

Aliphatic carbodi-imides. III. E. Schmidt and W. Striewsky (*Ber.*, 1941, **74**, [*B*], 1285—1296; cf. A., 1943, II, 219).—The stability of NR:C:NR' towards storage and Na is increased by increase in mol. wt. and still more so if R or R and R' are *sec.* Prep. of NR:C:NR' is much improved by use of moist HgO, which reduces the amount of carbamide obtained as by-product. The

following are described: di-*n*-, b.p. 53—54°/10 mm., and -iso*propyl*-, b.p. 36—37°/10 mm., N-n-*propyl*-N'-iso*propyl*-, b.p. 45°/10 mm., -N'-cyclo*hexyl*-, b.p. 105—106°/10 mm., and -N'-*γ-dimethylamino*-n-*propyl*-, b.p. 99—101°/10 mm. (*methiodide*, m.p. 98·5—99·5°), N-iso*propyl*-N'-cyclo*hexyl*-, b.p. 97—98°/10 mm., -N'-n-*dodecyl*-, b.p. 169—170·5°/10 mm., and -N'-*γ-dimethylamino*-n-*propyl*-, b.p. 91—92°/10 mm. (*methiodide*, m.p. 108—109°), and N-*methoxymethyl*-N'-*γ-dimethylamino*-n-*propyl*-, b.p. 105—106°/10 mm. (*methiodide*, m.p. 89—90°), *-carbodi-imide*; N-n-*propyl*-N'-iso*propyl*-, m.p. 90—91°, -N'-cyclo*hexyl*-, m.p. 88·5—89·5° (~103° after resolidification), and -N'-*γ-dimethylamino*-n-*propyl*-, an oil (*picrate*, m.p. 155·5—156·5°), NN'-*di*iso*propyl*-, m.p. 141—141·5° (lit. 161°), N-iso*propyl*-N'-cyclo*hexyl*-, m.p. 139—140°, -N'-n-*dodecyl*-, m.p. 74·5—75·5°, and -N'-*γ-dimethylamino*-n-*propyl*-, m.p. 79—80° (*picrate*, m.p. 158—159°), and N-*methoxymethyl*-N'-*γ-dimethylamino*-n-*propyl*-, m.p. 56·5—58·5°, *-thiocarbamide*. OH·[CH$_2$]$_2$·NH$_2$ and CH$_2$:CH·CH$_2$·NCS in cold CHCl$_3$ give N-*β-hydroxyethyl*-N'-*allylthiocarbamide*, m.p. 77·5—78·5°, which with HgO in H$_2$O gives, by ring-closure of the carbodi-imide, 2-allylimino-oxazolidine, b.p. 104—105°/10 mm. (*picrate*, m.p. 146—147°). N-*γ-Hydroxy*-n-*propyl*-N'-*allylthiocarbamide*, m.p. 58—59°, with moist HgO in Et$_2$O or C$_6$H$_6$ gives similarly *2-allyliminotetrahydro*-1 : 3-*oxazine*, b.p. 101·5—103°/10 mm. (*picrate*, m.p. 132—133°). R. S. C.

Acrylonitrile. V. Cyanoethylation of aldehydes. H. A. Bruson and T. W. Reiner (*J. Amer. Chem. Soc.*, 1944, **66**, 56—58; cf. A., 1943, II, 122, 153).—CHEt$_2$·CHO or CHEtBu·CHO with CH$_2$:CH·CN in 50% KOH at 55—58° gives *γ-aldehydo-γ-ethyl*-n-*hexonitrile* (**I**) (76·6%), b.p. 128°/4 mm., or -n-*octonitrile* (**II**) (79·5%), b.p. 140—142°/5 mm., respectively, hydrolysed by boiling 10% NaOH to *γ-aldehydo-γ-ethyl*-n-*hexoic* (**III**), b.p. 142°/3 mm., and -n-*octoic acid* (**IV**), b.p. 157°/4 mm. Air, H$_2$O$_2$, or KMnO$_4$ oxidises (**III**) and (**IV**) to *αα-diethyl*-, m.p. 84°, and *α-ethyl-α*-n-*butyl-glutaric acid* (**V**), m.p. 81—82°, respectively. The CHO of (**I**) and (**II**) resists alkali but is oxidised in air; thus, (**I**) yields *γ-carboxy-γ-ethyl*-n-*hexonitrile*, m.p. 88°. H$_2$–Raney Ni converts (**II**) and (**IV**) in aq. NaOH into the *lactones*, b.p. 101°/2·5 mm. and (**VI**) 124°/3·5 mm., of γ-hydroxymethyl-γ-ethyl-*n*-hexoic and -*n*-octoic acids, respectively.
CHPr^a:CEt·CHO and CH$_2$:CH·CN give, with migration of H, *γ-aldehydo-γ-ethyl*-Δ^δ-n-*octenonitrile*, b.p. 138—140°/6 mm., and -n-*octenoic acid* (**VII**), b.p. 154°/4 mm. Hydrogenation of (**VII**) gives (**VI**) and oxidation gives (**V**). R. S. C.

II.—SUGARS AND GLUCOSIDES.

Blood-sugars. IV. Effect of mercury on the reducing power of dilute solutions of glucose. M. Lora Tamayo and J. M. Pinar Miura (*Anal. Fis. Quím.*, 1940, **36**, 132—140).—Dil. solutions of glucose are oxidised by HgCl$_2$ in NaOH to AcOH and H$_2$C$_2$O$_4$. Acid solutions remain unchanged. F. R. G.

Formation of anhydro-derivatives by the action of alkali on mononitrate acetates of glucose and methylglucoside. E. K. Gladding and C. B. Purves (*J. Amer. Chem. Soc.*, 1944, **66**, 76—81).—In the sugar series, the behaviour of nitrates towards alkali resembles that of halides, methane- or *p*-toluene-sulphonates: fission is normally >CH·O·NO$_2$ → >CH·OH + HNO$_3$, but, if the NO$_2$ is "blocked," some reaction CH$_2$R·O·NO$_2$ → RCHO + HNO$_2$ occurs. *α-D*-Glucopyranose 2 : 3 : 4 : 6-tetra-acetate 1-nitrate (**I**), m.p. 148—149° (corr.), $[\alpha]_D^{20}$ +148° in CHCl$_3$, is obtained by nitrating *β*-glucose penta-acetate in CHCl$_3$; the NO$_2$ is as labile towards alkali as are the Ac; with NaOMe–MeOH it gives 75% of a CHCl$_3$-sol. material which, after re-acetylation, on one occasion crystallised to an inseparable mixture, on another yielded 28% of *β*-methylglucoside tetra-acetate (**II**), and probably consists of a 1 : 1 mixture of (**II**) and glucosan<1 : 5>*β*<1,6> triacetate (**III**); with NaOH in aq. dioxan it gives 33% of (**III**), 4·5% of HNO$_2$, and ~66% of a gum. The NO$_2$ of *β*-methylglucoside 3 : 4 : 6-triacetate 2-nitrate (**IV**) is removed rather faster than is that of (**I**); with NaOH in aq. dioxan gives only 2·3% of HNO$_2$ with 84% of mixed anhydromethylhexosides, $[\alpha]_D^{20}$ −111° to −106° in H$_2$O (a fraction having m.p. 127—136° was isolated), containing >6% of methylhexosides. Consecutive methylation, nitration, and treatment with boiling BaCO$_3$–MeOH converts *D*-glucosan<1,5>*β*<1,6> into 2 : 3 : 4-trimethyl-*β*-methyl-*D*-glucopyranosidyl 6-nitrate (50%), m.p. 52—54° (corr.), $[\alpha]_D$ −7° in CHCl$_3$, which is more stable towards alkali than is (**I**) or (**IV**); NaOH in 50% aq. MeOH at 60° yields 75% of 2 : 3 : 4-trimethyl-*β*-methylglucoside, 20% of HNO$_2$, and 20% of an acidic, methylated tar. R. S. C.

α-Methylglucopyranoside 2 : 3 : 4-triacetate 6-nitrate and β-methylpyranoside 3 : 4 : 6-triacetate 2-nitrate. E. K. Gladding and C. B. Purves (*J. Amer. Chem. Soc.*, 1944, **66**, 153—154).—*α*-Methylglucoside 6-CPh$_3$ ether 2 : 3 : 4-triacetate (modified prep.), new m.p. 143—145° (corr.), with P$_2$O$_5$–HNO$_3$ at 3—5° gives *α-methylglucoside* 2 : 3 : 4-*triacetate* 6-*nitrate* (88%), m.p. 112—113° (corr.), $[\alpha]_D^{20}$ +132° in CHCl$_3$, also obtained from the 6-iodide by AgNO$_3$ (excess) in hot MeNO$_2$ and converted thereinto by NaI in (CH$_2$Ac)$_2$. *β*-Methylglucoside 3 : 4 : 6-triacetate (modified prep.) gives similarly its *2-nitrate*, m.p. 117—118° (corr.), $[\alpha]_D^{25}$ −1° in CHCl$_3$. R. S. C.

Glucose 6-fluorohydrin and its derivatives. B. Helferich and A. Gnuchtel (*Ber.*, 1941, **74**, [*B*], 1035—1039).—*α*-Methylglucoside tetramethanesulphonate and KF in boiling H$_2$O (30% yield) or, better, MeOH at 100° (tube) give *α-methylglucoside* 6-*fluoride* 2 : 3 : 4-*trimethanesulphonate*, m.p. 133—134°, $[\alpha]_D^{22}$ +93·1° in C$_5$H$_5$N, but the MeSO$_2$ cannot be removed without affecting the F. *α*-Methylglucoside 2 : 3 : 4-triacetate 6-methanesulphonate and KF give only glucose and derivatives of anhydroglucose. 3 : 5-Benzylidene-1 : 2-*iso*propylideneglucopyranose 6-methanesulphonate and KF,2H$_2$O in MeOH at 100° give 3 : 5-*benzylidene*-1 : 2-iso*propylideneglucofuranose* 6-*fluoride* (96%), m.p. 104—105° (corr.), $[\alpha]_D^{21}$ +14·2° in C$_6$H$_6$, whence H$_2$SO$_4$–MeOH–H$_2$O at the b.p. and then Ac$_2$O–C$_5$H$_5$N at 100° gives *glucose* 6-*fluoride* 1 : 2 : 3 : 4-*tetra-acetate* (45%), m.p. 125—126°, $[\alpha]_D^{19}$ +20·1° in C$_5$H$_5$N. H$_2$SO$_4$–MeOH–H$_2$O then yields *glucose* 6-*fluoride* (>60%), sinters ~145°, m.p. 155°, $[\alpha]_D^1$ +85·8° → +46·8° in H$_2$O, whilst HBr in AcOH and then AcOH–CHCl$_3$ gives 1-*bromoglucose* 6-*fluoride* 2 : 3 : 4-*triacetate* (**I**), m.p. 127—128° (corr.), $[\alpha]_D$ +234° in CHCl$_3$. PhOH and Ag$_2$O in quinoline convert (**I**) into *phenyl-β*-d-*glucoside* 6-*fluoride* 2 : 3 : 4-*triacetate*, m.p. 167—168° (corr.), $[\alpha]_D^1$ −8·2° in CHCl$_3$, and thence (NaOMe) *phenyl-β*-d-*glucoside* 6-*fluoride*, m.p. 148—149° (corr.), $[\alpha]_D^2$ −79·0° in H$_2$O. Vanillin, (**I**), and NaOH in aq. COMe$_2$ at room temp. give *vanillyl-β*-d-*glucoside* 6-*fluoride*, m.p. 181—182° (corr.), $[\alpha]_D^{20}$ −48·6° in C$_5$H$_5$N, by way of its *triacetate*, m.p. 166—167° (corr.), $[\alpha]_D^{20}$ −35·7° in CHCl$_3$. R. S. C.

Glucoside of a γ-hydroxy-carboxylic acid. B. Helferich, W. Richter, and H. Flechsig (*Ber.*, 1941, **74**, [*B*], 1019—1022).—Acetobromoglucose, CMe$_2$:CH·[CH$_2$]$_2$·CHMe·OH, CaSO$_4$, and Ag$_2$O in CHCl$_3$ give mixed diastereoisomerides, whence ~11% of *ζ-methyl-β-Δ^ε*-n-*heptenylglucoside tetra-acetate*, m.p. 93—94°, $[\alpha]_D^{16}$ −2·8° in CHCl$_3$, is obtained. With boiling NaOMe–MeOH this gives the free *glucoside* (**I**), m.p. 78—79°, $[\alpha]_D^{16}$ −23° in H$_2$O, and with O$_3$–AcOH, followed by Zn dust in Et$_2$O–AcOH, gives *γ-glucosidoxy*-n-*valeraldehyde tetra-acetate* (~65%), m.p. 128—129°, $[\alpha]_D^{22}$ −0·5° in CHCl$_3$ (*semicarbazone*, m.p. 108—109°, $[\alpha]_D^{20}$ −2·3° in CHCl$_3$; 2 : 4-dinitrophenylhydrazone, m.p. 170°), oxidised by KMnO$_4$–COMe$_2$ at ~2° to *γ-glucosidoxy*-n-*valeric acid tetra-acetate* (60%), m.p. 92—93°, *α* 0 (*Me* ester, m.p. 85—86°, *α* 0). The rate of hydrolysis of (**I**) by emulsin is reduced to about one seventh by conversion into the aldehyde. R. S. C.

Nature of erythroamylose particles and of higher dextrins produced by α-diastase.—See A., 1944, III, 432.

Relation of starch–iodine absorption spectra to the structure of starch and starch components. R. R. Baldwin, R. S. Bear, and R. E. Rundle (*J. Amer. Chem. Soc.*, 1944, **66**, 111—115).—The position of the max. and val. of $\varepsilon_{max.}$ of the absorption spectra of starch–I complexes (0·01% solution) differentiate amyloses from amylopectins, but cannot be used to analyse whole starch owing to variation among amyloses and amylopectins from different starches. The amount of I bound increases as the [KI] decreases, becoming 1 I per ~6 glucose units at infinitely small [KI]. Increase in chain-length of amylose or in length of the unbranched portion of amylopectin shifts the max. to longer λ and increases ε; both phenomena, particularly ε, may be used to determine mol. wts. and degrees of branching, giving vals. in agreement with other methods. The spectrometric method shows higher vals. for bound I than does potentiometric titration, owing to rapid removal of I from the ends of the helices during the titration. R. S. C.

Effect of acid hydrolysis on activity of polysaccharides in enzymic synthesis of starch.—See A., 1944, III, 500.

Influence of dextrin on synthetic action of plant phosphorylase.—See A., 1944, III, 500.

Cellulose and liquid hydrogen chloride. Influence of morphological structure and crystal lattice structure on the reaction and activity of cellulose. M. Ulmann and K. Hess (*Ber.*, 1941, **74**, [*B*], 1465—1473).—The reaction velocity of ramie cellulose (**I**) with liquid HCl at −15° to 20° is given, up to 66% completion, by $dx/dt = K(a - x)/l$, in which l measures diffusion of HCl into the (**I**); l can be represented as $K'\sqrt{t}$, whence for the whole reaction $K = 0{\cdot}5\sqrt{t}\log_e a(a - x)$. After 66% completion of the reaction (for which $K = 0{\cdot}058$), the velocity suddenly increases, proceeding then to 100% completion. When ground in a "swinging" mill, (**I**) reacts much faster ($K = 0{\cdot}103$) up to 58% completion; a similar sudden increase in reaction rate then occurs. The non-reducing portion remaining from partly reacted ground (**I**) consists of unchanged (**I**) and H$_2$O-sol. cellulose (**II**); the amount of (**II**) is const. (25%) until shortly after the sudden increase in velocity but then falls gradually to approx. nil. When ground (**I**) is boiled in H$_2$O for 1 hr. and the suspension is then evaporated and dried at 105°, a "recryst." cellulose (**III**) is obtained, which reacts with HCl initially at the same rate ($K = 0{\cdot}060$) as does natural (**I**); a sudden increase in velocity occurs after 40% completion; 8% of (**II**) is also formed from (**III**), this amount remaining const. for a long time. (**III**) may also be prepared without heating, by drying the H$_2$O-treated (**I**) with EtOH and Et$_2$O. The amount of reaction is determined by the Bertrand reducing val.; results by Willstatter

and Schudel's method are more erratic. The *X*-ray diagram of (I) remains normal up to 66% reaction and thereafter is that of an amorphous substance; *X*-ray diagrams of (II) and (III) are both the same as that of "cellulose hydrate." The following interpretations are offered. The effect of grinding on the initial velocity, being reversible by H_2O, is due to lattice distortion; subdivision proceeds only to the individual fibrils. Also formation of (II), largely reversible by H_2O, occurs from lattices deformed by grinding. The sudden increase in velocity is due to HCl penetrating through less reactive layers (which react more slowly) and suddenly exposing normally reactive portions. R. S. C.

Cellulose–water adsorption isotherm.—See A., 1944, I, 153.

Study of the amorphous portion of dry, swollen cellulose by an improved thallous ethoxide method. A. G. Assaf, R. H. Haas, and C. B. Purves (*J. Amer. Chem. Soc.*, 1944, **66**, 59—65).—The no. of accessible OH in cellulose is determined by treatment with TlOEt in a solvent and then with MeI–C_6H_6 and determining the OMe in the product. When hydrocarbons (*n*-C_7H_{16}, -$C_{16}H_{22}$, -$C_{16}H_{34}$) are used as solvent, the % OMe is const., but when ethers [Et_2O, Pr_2O, Bu_2O, $(C_5H_{11})_2O$] are used, the % OMe ∝ the mol. vol. of the solvent ether. The % "amorphous" cellulose is defined as the % wetted by an ether of zero mol. vol., estimated by extrapolation from the ether graph. Thallation in alcohols is probably accompanied by swelling but confirms the results within ±10%. Unswollen linters contains only 0·25—0·5% of amorphous cellulose, but swollen linters contains up to 27±2%; the corresponding colloidal surfaces are 10—520 × 10^4 sq. cm. per g. R. S. C.

III.—HOMOCYCLIC.

Spectroscopic evidence for conjugation in *cyclo*propane systems. I. M. Klotz (*J. Amer. Chem. Soc.*, 1944, **66**, 88—91).—Hyperconjugation of a *cyclo*propane ring with an ethylenic linking causes some absorption due to resonance, so that absorption spectra are intermediate between those of systems containing C·C·C:C or C:C·C:C. Examples are Δ^6-*i*-cholestadiene, *i*-cholesteryl Me ether, *i*-cholestenone, and carone. The same principle may apply to terpenes containing *cyclo*butane rings. R. S. C.

Poly*cyclo*pentyls. J. von Braun and (Frl.) J. Reitz-Kopp (*Ber.*, 1941, **74**, [*B*], 1105—1110).—n-*Heptyl*-Δ¹-cyclo*pentene*, b.p. 102°/15 mm., is obtained (Grignard) from *n*-$C_7H_{15}Br$ and Δ^2-*cyclo*pentenyl chloride (I) in nearly 50% yield and is freed from halogen by Na at 100°. With fuming HBr (excess) at 100° or room temp. it gives 3-*bromo*-n-*heptyl*cyclo*pentane* (II) (>70%), b.p. 97—102°/0·2 mm., which reacts more slowly than does the Et analogue with Mg (A., 1937, II, 404), yielding after treatment with solid CO_2 3-n-*heptyl*cyclo*pentane*-1-*carboxylic acid* (22%), b.p. 186—188°/13 mm., and 3 : 3′-*di*-n-*heptyldi*cyclo*pentyl* (III) (~10%), b.p. 230°/13 mm. ~30% of (II) is obtained from (I) by Na wire and a little EtOAc in Et_2O at room temp. and then the b.p. 3-*cyclo*Pentenyl-1-ethyl*cyclo*pentane, b.p. 75—85°/12 mm. [obtained (34%) from Mg 3-ethyl*cyclo*pentyl bromide and (I)], with fuming HBr at room temp. gives 3-bromo-3′-ethyldi*cyclo*pentyl (IV) (77%), b.p. 135°/16 mm., which with Mg and then CO_2 gives impure 3-ethyldi*cyclo*pentyl-3′-carboxylic acid, b.p. ~130°/0·1 mm., and 3 : 3′-*diethylquater*cyclo*pentyl* (~10%), b.p. 160—170°/0·3 mm. [obtained in 20% yield from (IV) by Na]. The similarity in reactions of (II) and (IV), which contain the same no. of C, is noted. Mg 3-di*cyclo*pentylyl bromide and (I) give, after treatment with Na, Δ-*tri*cyclo*pentylene* [3-Δ²′′-cyclo*pentenyldi*cyclo*pentyl*] (V) (nearly 20%), b.p. 139—140°/10 mm., and quater*cyclo*pentyl (12%), b.p. 205—207°/9 mm. H_2–Pd in MeOH reduces (V) to *tri*cyclo*pentyl* (92%), b.p. 144°/12 mm. HBr converts (V) into 3-*bromotri*cyclo*pentyl* (~50%), b.p. 182°/10 mm., yielding with Na in Et_2O *hexa*cyclo*pentyl* (almost 40%), b.p. 235°/0·1 mm., of which 10% is obtained having m.p. 143—146°. *d* and *n* of poly*cyclo*pentyls increase regularly, but the b.p. show signs of alternation. In the above compounds the *cyclo*pentyl nuclei are united in the 1 : 3-positions. R. S. C.

Reactions of *cyclo*hexane and decahydronaphthalene under hydrogenation-cracking conditions.—See B., 1944, II, 125.

Chlorination of *cyclo*hexane.—See B., 1944, II, 128.

Rubber, polyisoprenes, and allied compounds. VI. Mechanism of halogen-substitution reactions and the additive halogenation of rubber and of dihydromyrcene. G. F. Bloomfield. **VII. Action of nitric oxide thereon.** G. F. Bloomfield and (in part) G. A. Jeffrey (*J.C.S.*, 1944, 114—120, 120—124; cf. A., 1943, II, 289).—Chlorination of peroxide-free *cyclo*hexene (I) by Cl_2 or SO_2Cl_2 gives substituted and additive derivatives, the former retaining full unsaturation. (I) with Cl_2 yields *cyclo*hexene, mono- (II), 1 : 2-di- (III), and tri-chloro*cyclo*hexane, b.p. 52—53°/0·01 mm. Comparison of the reactions of (II) and 1-chloro*cyclo*hexene (from *cyclo*hexanone and PCl_5) towards $AgNO_3$ in EtOH and to ICl suggests that (II) is a mixture of 3- (IV) and 4-chloro*cyclo*hexene (20%). SO_2Cl_2 with (I) in presence of peroxide gives (III) but with peroxide-free (I) in presence of quinol gives (III) and (IV) and the *chloride* of 2-chloro*cyclohexyl sulphite*, b.p. 74°/0·002 mm., which with H_2O yields 2-chloro*cyclo*hexanol and *bis*-(2-*chloro*cyclo*hexyl*) *sulphite* (?), m.p. 92°. SO_2Cl_2 and (I) with a little I at 80° give (III) and (IV). SO_2Cl_2 (1 mol. per 4 :) and dihydromyrcene (V) in presence of Bz_2O form the *dichloride*, b.p. 55—56°/0·2 mm., but SO_2Cl_2 (2 mol.) and (V) (1 mol.) give (Bz_2O present) the *tetrachloride*, b.p. 82—90°/0·002 mm., m.p. 50°. Rubber (VI) with SO_2Cl_2 and Bz_2O gives *polyisoprene dichloride*, $(C_5H_8Cl_2)_n$, indistinguishable from material obtained from (VI) and PhICl$_2$. (V) with $(CH_2{\cdot}CO)_2NBr$ (VII) gives *monobromodihydromyrcene*, b.p. 54°/0·1 mm. (VI) and (VII) (0·5 Br per C_5H_8 unit) yield a *compound*, $(C_{10}H_{15}Br)_n$, without formation of HBr. (VI) gives an entirely additive reaction with Br at 0° (if a little EtOH is present in the solvent, *e.g.*, $CHCl_3$, used) and a method based on Br addition can be used for determination of rubber hydrocarbon. The reaction mechanism of chlorination of (VI) is discussed, and it is suggested that provision of Cl in free radical form is necessary for a wholly additive reaction. The reaction of mol. Cl_2 or Br is explained by formation of an activated dihalide, further products being determined by the nature of the olefinic system and the experimental conditions.

VII. In the reaction of NO with (I), 1-methyl*cyclo*hexene (VIII), (V), and (VI) the general characteristics of a free-radical chain mechanism are exhibited. The induction period (15—30 min.) varies with the light intensity. N_2 which is formed stops the reaction, but if removed >1 mol. of NO per : is absorbed, 1/3—1/4 vol. of N_2 being evolved per vol. of NO absorbed. Products contain N (generally linked to C) in various states of combination with O. It is suggested that NO is converted into higher oxides of N (in the liquid phase only) by a mechanism involving the hydrocarbon, and HNO_3 or N_2O_3 was detected. The apparatus used is described. (I) (1 mol.) absorbs NO (1·6 mols.) to give the *ψ*-nitrosite, m.p. 153° (decomp.), for which a bimol. structure is confirmed by *X*-ray examination, a mixture of 1-nitro*cyclo*hexene (giving adipic acid on oxidation, and *cyclo*hexanoncoxime on reduction) and 3-nitro*cyclo*hexene (?), and an *oil* (IX), $C_6H_{10}O_{3\cdot6}N_{1\cdot6}$, containing N and O added or substituted at the original (IX) gives a *compound*, $C_6H_8O_3N_2$, m.p. 107—108°, with KOH, and on oxidation ($KMnO_4$) gives adipic acid and a neutral oil. (V) (1 mol.) absorbs NO (0·73 mol.) and evolves N_2 (0·22 mol.) giving a *nitrodihydromyrcene* (?), b.p. 60—70°/0·001 mm., and a *solid*, $C_{10}H_{18}O_{3\cdot3}N_{1\cdot8}$. (VIII) gives a *nitromethyl*cyclo*hexene* (?), b.p. 50°/0·01 mm., and a viscous residue. The properties of the products obtained from (VI) for absorption of various amounts of NO are tabulated. No definite compounds were isolated. D. G.

***cis–trans*-Isomerisation and *cis*-peak effect in the α-carotene set and in other stereoisomeric sets.** L. Zechmeister and A. Polgár (*J. Amer. Chem. Soc.*, 1944, **66**, 137—144).—The ethylenic linkings of carotene etc. are numbered serially, no. 1 being that in the *β*-ionone ring. *cis*-Linkings are indicated by prefixes, *e.g.*, 3 : 6-di-*cis*- indicates that ethylenic linkings nos. 3 and 6 are *cis*. In α-carotene (I), nos. 3, 5, 6, 7, and 9 can be *cis* and 32 stereoisomerides are possible. By boiling or illumination in light petroleum, by treating in light petroleum with I (in light), 10% HI, or 37% HCl, or by melting, (I) gives varying amounts of the following neo-α-carotenes, listed in order of decreasing adsorption affinity with absorption max. (A. in light petroleum) in parentheses: U (4710, 4415), V (4655, 4370), W (4705, 4410), X (4635, 4350), Y (4675, 4370), all *trans*-α-carotene (4770, 4465), A (4685, 4390), B (4665, 4370), C (4725, 4425), D (4600, 4320), and E (4615, 4335). U, m.p. 65° (corr.), $[\alpha]_{Cd}^{25}$ +221°±5% in C_6H_{14}, and W, m.p. 97° (corr.), $[\alpha]_D$ +365° in light petroleum, are obtained cryst. (photomicrographs). Absorption data (partly new) are interpreted to indicate the following configurations: U 9-*cis*, W 3-*cis*, V 3 : 9-di-*cis*, A (? 7 :)9-di-*cis*, C 6- or 5-*cis*, B 5 : 9- or 6 : 9-di-*cis*, A and B being chosen from 5 : 9-, 6 : 9-, and 3 : 6-di-*cis*; neolutein A 6- or 5-*cis*, B 3- or 9-*cis*; neolycopene A 6-*cis*., B 1 : 6- or 3 : 6-di-*cis*. R. S. C.

Alkylation of *o*- and *p*-xylene. D. Nightingale and J. R. Janes (*J. Amer. Chem. Soc.*, 1944, **66**, 154—155).—With $Bu^{\gamma}Cl$–$FeCl_3$ or $Bu^{\gamma}OH$–BF_3, *o*-xylene gives good yields of 1 : 2 : 4-$C_6H_3Me_2Bu^{\gamma}$ (oxidised to 2 : 4 : 1-$C_6H_3MeBu^{\gamma}{\cdot}CO_2H$). *p*-Xylene does not condense with $Bu^{\gamma}OH$–80% H_2SO_4, $Bu^{\gamma}Cl$–$FeCl_3$, or $CMe_2{:}CH_2$–$FeCl_3$, and with $Bu^{\gamma}OH$–BF_3 gives an inseparable mixture. PhMe is readily alkylated by $CMe_2{:}CH_2$–$FeCl_3$. R. S. C.

Delay in the heat-polymerisation of styrene caused by *p*-benzoquinone. J. W. Breitenbach and K. Horeischy (*Ber.*, 1941, **74**, [*B*], 1386—1389).—When styrene is heated with 2 mol.-% of *p*-O:C_6H_4:O (I) at 120°, quinhydrone can be isolated from the product. Polymerisation is not prevented by (I) but leads to products of quite low *η* and mol. wt., which invalidates the conclusions of Foord (A., 1940, I, 167). R. S. C.

Alkylation by olefines in presence of aluminium chloride. I. S. I. Lurie and A. J. Golovatscheva (*J. Gen. Chem. Russ.*, 1943, **13**, 189—194).—*m*-Xylene and $CMe_2{:}CH_2$ at 12—14° in presence of $AlCl_3$ in EtBr afford 1 : 2 : 4-$C_6H_3Me_2Bu^{\gamma}$ in 18% yield. Various activators (HCl, $CHCl_3$, CCl_4) raise the yield, the most active being CCl_4 (60%). With alkoxybenzenes the ·CH: groups act as promoters

of the reaction, rendering the presence of added activators unnecessary. R. T.

Hydrolytic rupture of carbon linkings. VI. Substituted stilbenes. M. M. Schemjakin and N. I. Oranski (*J. Gen. Chem. Russ.*, 1943, **13**, 175—183).—Substituted stilbenes are hydrolysed by aq. alkalis as follows: CHR:CHR′ + H_2O → R·CHO + R′Me [R = R′ = Ph, *o*-NO_2·C_6H_4·; 2 : 4-$C_6H_3(NO_2)_2$, 2 : 4-NO_2·C_6H_3·SO_3H; R = *o*-NO_2·C_6H_4, R′ = 2 : 4-$C_6H_3(NO_2)_2$; R = Ph, R′ = 2 : 4-$C_6H_3(NO_2)_2$]. The velocity of the reaction rises with increasing asymmetry of the mol. R. T.

Physical data of αα-diphenyl-alkenes and -alkanes and ααωω-tetraphenylalkenes. A. W. Schmidt and C. Hartmann (*Ber.*, 1941, **74**, [*B*], 1325—1332).—By interaction of $MgPhBr$ with RCO_2Et or $X(CO_2Et)_2$ and subsequent dehydration by $KHSO_4$ are prepared *αα-diphenyl-*Δ^{α}-n-*butene*, b.p. 108—110°/4 mm., *-octene*, m.p. −5·5° to −6°, b.p. 133—134°/0·05 mm., *-dodecene*, m.p. 5—6°, b.p. 170—171°/0·05 mm., *-hexadecene*, m.p. 25·5°, b.p. 196—197°/0·04 mm., and *-octadecene*, b.p. 202—203°/0·04 mm., $(CPh_2{:}CH{\cdot}[CH_2]_n)_2$ in which *n* = 1 m.p. 108°, and 2 m.p. 113° (lit. 92—93°), *αακκ-tetraphenyl-*$\Delta^{\alpha\iota}$-n-*decadiene*, m.p. 113°, and *ααωω-tetraphenyl-*$\Delta^{\alpha\rho}$-n-*octadiene*, m.p. 77°. H_2–Pd–$BaSO_4$ in Et_2O or EtOH then yields αα-diphenyl-*n*-butane, b.p. 103—104°/0·05 mm., -octane, m.p. −5° to −4°, b.p. 143—145°/0·1 mm., and -hexadecane, m.p. 26°, b.p. 211—213°/0·1 mm., and *αα-diphenyl*-n-*hexadecan-α-ol*, m.p. 48—49°. *n*, *d*, and *η* are also recorded for the hydrocarbons. R. S. C.

Magnetic investigations of organic substances. XXI. Diradicaloid terphenyl derivatives. XXII. Diradicaloid quaterphenyl derivative. E. Muller and H. Pfanz (*Ber.*, 1941, **74**, [*B*], 1051—1074, 1075—1083).—XXI. *p*-$C_6H_4Ph_2$, *p*-C_6H_4Ph·COCl, and $AlCl_3$ at 190—200° give, after sublimation of the product, 4 : 4″″-*di*-p-*phenylbenzoyl*-*p-terphenyl* (20%), m.p. 406—408°. This is finely powdered, stirred in molten $C_{10}H_8$–N_2, diluted with C_6H_6, and treated with *p*-Li·C_6H_4Ph–Et_2O–N_2 at 25—30° [at 70° much (*p*-$C_6H_4Ph)_n$ is formed], thus yielding 4 : 4″″-*bis*-(*α-hydroxydi*-p-*xenylmethyl*)-p-*terphenyl* (58%), sinters from ~140°, m.p. 165—175°, resolidifies, remelts at ~283—286° (violet-blue in H_2SO_4), which with gaseous HCl in boiling C_6H_6–AcOH gives the *dichloride* (54%), sinters from 165°, m.p. 185°, resolidifies, remelts at ~294—296°, whence Cu-bronze or "mol." Ag in C_6H_6–N_2 at 80° yields 4 : 4″″-p-*terphenylenebisdi*-p-*xenylmethyl* (I) (peroxide). Similarly are prepared 4 : 4″″-dibenzoyl-, m.p. 296—297°, 4 : 4″″-*bis*-(*α-hydroxy-α*-p-*xenylbenzyl*)-, sinters 100°, m.p. 150—~245° (greenish-blue in conc. H_2SO_4), 4 : 4″″-*bis*-(*α-chloro-α*-p-*xenylbenzyl*)- (prep. by gaseous HCl in, successively, MeOH–C_6H_6, AcCl–C_6H_6, and AcCl–C_6H_6–Et_2O), sinters from 270°, m.p. 282—283°, 4 : 4″″-*bis*-*α-hydroxybenzhydryl*- (II), +C_6H_6, sinters 130°, m.p. ~160—165°, and solvent-free, m.p. 207·5—209·5° (reddish-violet in H_2SO_4), and 4 : 4″″-*bis*-*α-chlorobenzhydryl*-, m.p. 248—249°, -p-*terphenyl* and 4 : 4″″-p-*terphenylenebis-phenyl*-p-*xenylmethyl* (III) (peroxide) and *-diphenylmethyl* (IV), sinters 135—140°, m.p. 165—200° (N_2) (di- or poly-meric *peroxide*). Structures are confirmed by absorption spectra of Ph_2, *p*-$C_6H_4Ph_2$, CPh_3·OH, *p*-$C_6H_4(CPh_2{\cdot}OH)_2$ [max. at ~2640 A. (log ε 3·12)], (*p*-OH·CPh_2·C_6H_4·)$_2$ [max. at 2630 A. (log ε 4·52)], and (II) [max. at 2920 A. (log ε 4·7)] in dioxan; changes in $\lambda_{max.}$ are regular. $\chi_{mol.}$ are recorded for the diketones, dicarbinols, dichlorides, (I), (III), and (IV) in C_6H_6, and for solid (I) and (IV). (I), (III), and (IV) are paramagnetic in C_6H_6 at 18° and 80° and when solid. For (I) the apparent % of diradical in 1·8% C_6H_6 solution is 53—54±5 at 18° and 80°; for (III) and (IV) it is less and varies with concn. and temp.; heats of dissociation are (I) 0±2·5, (III) −8·3±2·5, and (IV) −9·5±2·5 kg.-cal. are (I) 0·78 at −183° to 0·81 at 20° and (IV) 0·51 at −183° to 20°, rising to 0·65 at 120°, and then falling to 0·35 at 180°. The compounds, (I), (III), and (IV) are held to be "diradicaloid," *i.e.*, prevented from acting as 100% free radicals by the fact that free rotation around a long X in CR_2·X·CR_2 prevents completely planar configuration. (IV) is ∉ dimeric in C_6H_6, which is considered to be due to association to large rings.

XXII. 4 : 4‴″-*p*-Quaterphenylenebisdiphenylmethyl (V) is diradicaloid. By the methods described above (*p-p′*-$C_6H_4Ph)_2$ (VI) gives 4 : 4 *-dibenzoyl-* (49%), m.p. 357—359°, 4 : 4‴″-*bis-α-hydroxybenzhydryl-* (VII), sinters ~120°, m.p. 220—221°, and 4 : 4‴″-*bis-α-chlorobenzhydryl*-p-*quaterphenyl*, m.p. 263—264°, and (V). (VII) is greenish-blue in H_2SO_4 and has an absorption max. at 3090 A. χ are recorded for (VI) and the products. (V) is paramagnetic, has heat of dissociation −7·3±2·5 kg.-cal., $\mu_{eff.}$ 0·81 at 20° and 1·23 at 80°, and in C_6H_6 an apparent diradical content 15·5±3% at 20° and 19·0±3% at 80°. (V) is magnetically anisotropic. It is very highly electrified by friction; the charge is dissipated when the surrounding air is ionised by Ra. R. S. C.

***pp′*-Diphenyl diradical of the triphenylmethyl type. III.** W. Theilacker (*Ber.*, 1941, **74**, [*B*], 1353—1359).—Polemical against Muller (cf. preceding abstract). Association of *pp′*-diradicals, $\cdot C_6H_4{\cdot}C_6H_4{\cdot}$, to dimerides is extremely improbable on steric grounds. Dissociation of such radicals (if formed) is more complicated than Müller assumes, since partial dissociation to $\cdot[C_6H_4]_4\cdot$ gives a paramagnetic mol. The solids are probably long-chain structures formed by polymerisation. R. S. C.

Syntheses of compounds related to vitamin-*K*. I. Synthesis of 2-methylnaphthalene. E. J. H. Chu and Z. I. Shen (*J. Chinese Chem. Soc.*, 1943, **10**, 119—113).—PhMe, $(CH_2{\cdot}CO)_2O$, and $AlCl_3$ yield *p*-$C_6H_3Me{\cdot}CO{\cdot}[CH_2]_2{\cdot}CO_2H$, m.p. 126·2—127·3°, reduced (Clemmensen) to *p*-$C_6H_4Me{\cdot}[CH_2]_3{\cdot}CO_2H$, m.p. 56°, convertible through the chloride by $AlCl_3$ in PhMe at room temp. into 1-keto-7-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene, m.p. 33°, and thence (Clemmensen) 6-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene, b.p. 94—96°/10 mm. (some 3 : 4 : 3′ : 4′-*tetrahydro*-7 : 7′-*dimethyl*-1 : 1′-*dinaphthyl*, m.p. 162—163°, is isolated); S at 215—230° then gives 2-$C_{10}H_7Me$ (overall yield, 6%). A. T. P.

Triterpenes. LXXXVI. Birch-tar oil.—See A., 1944, II, 165.

New route to polycyclic compounds having an angular methyl group. Synthesis of *iso*chrysofluorene. N. N. Chatterjee and H. B. Roy (*J. Indian Chem. Soc.*, 1943, **20**, 329—330).—Et 2-methyl-*cyclo*hexanone-2-carboxylate with 1-$C_{10}H_7$·MgBr gave *Et* 1-*α-naphthyl*-2-*methylcyclohexanol*-2-*carboxylate*, b.p. 220—225°/6 mm., dehydrated ($SOCl_2$–C_5H_5N–Et_2O) to *Et* 1-*α-naphthyl*-2-*methyl*-Δ^6-*cyclohexene*-2-*carboxylate*, b.p. 210—220°/6 mm., which was reduced (H_2, PtO_2, EtOH) very slowly to *Et* 1-*α-naphthyl*-2-*methylcyclohexane*-2-*carboxylate*, b.p. 208—210°/6 mm. The free *acid*, b.p. 235—245°/7 mm., was converted into its acid chloride, which with $AlCl_3$ gave *methylhexahydroperibenzanthrone* (I), b.p. 215—225°/4 mm. Reduction of (I) (HI and red P) gave *methylhexahydroisochrysofluorene* (not isolated pure), which with Se gave *iso*chrysofluorene, m.p. 84° (picrate, m.p. 110—111°). D. G.

Perylene and its derivatives. LIV. Molecular compound of perylene with two molecules [four atoms] of iodine, $C_{20}H_{12},2I_2$. M. Pestemer and E. Treiber (*Ber.*, 1941, **74**, [*B*], 964—975).—Dependence of the saturation concn. on the composition of the solid phase in the system, perylene (I)–I–C_6H_6 or –$CHCl_3$, shows the existence of a *compound*, $C_{20}H_{12},4I$, forming mixed crystals with excess of I, in the solid phase (cf. Brass *et al.*, A., 1933, 57; 1939, II, 207). The solubilities and additivities of absorption spectra prove that the compound is ∉95% dissociated in solution. Absorption spectra are recorded for (I) and I in C_7H_{16} and in C_6H_6, and for Br, 3 : 9- and 3 : 10-dibromoperylene in *cyclo*hexane. R. S. C.

Fission of amines by alkali metals. E. Stoelzel (*Ber.*, 1941, **74**, [*B*], 982—986).—Amines, NRR'_2, are cleaved by K or K–Na in Et_2O at room temp. to $KR + KNR'_2$; products are identified by interaction with CO_2. Thus, NPh_2·CPh_3, NMe_2·CPh_3, or NH_2·CPh_3 gives CPh_3·CO_2H; NPh_2·CH_2Ph gives NPh_2·CO_2H and $NHPh_2$; *benzhydryldimethylamine* (prep. from $CHPh_2Br$ by $NHMe_2$ and then Na–Hg in C_6H_6–EtOH), m.p. 72°, or NH_2·$CHPh_2$ gives $CHPh_2$·CO_2H. R. S. C.

Analogues of pantothenic acid. IV. Aryl derivatives of pantoyltaurine. J. Barnett, D. J. Dupre, B. J. Holloway, and F. A. Robinson (*J.C.S.*, 1944, 94—96).—$CHPhCl{\cdot}CH_2{\cdot}NH_2,HCl$ (from $OH{\cdot}CHPh{\cdot}CH_2{\cdot}NH_2,HCl$ and $SOCl_2$) with Na_2SO_3 at 100° gives *α-phenyltaurine* (I), m.p. 258°. The Na salt of (I) with pantothenolactone gives the Na salt of *β-(α γ′-dihydroxy-β′β′-dimethylbutyramido)-α-phenylethanesulphonic acid* (II). *β-Hydroxy-αα-diphenylpropaldehyde*, m.p. 137—139° (from $CHPh_2$·CHO and CH_2O), is converted into its cyanohydrin, which is hydrolysed to dl-*α-hydroxy-ββ-diphenyl-γ-butyrolactone*, (III), two forms, m.p. 141° and 174°. (III) with the Na salt of taurine gives *β-(αγ-dihydroxy-ββ-diphenylbutyramido)ethanesulphonic acid* (IV). Pantothenolactone gives *mono*-p-*toluenesulphonylpantothenolactone*, m.p. 114—115°, which with the Na salt of taurine gives the Na salt of *β-(α*-p-*toluenesulphonyl-γ′-hydroxy-β′β′-dimethylbutyramido)ethanesulphonic acid* (V). (II), (IV), and (V) showed no bacteriostatic activity *in vitro* or *in vivo*. Prep. of *α-hydroxy-β-phenylisovaleric acid*, m.p. 94—95°, is described. D. G.

Action of nitrous acid on 4-dimethylaminodiphenyl. J. Guiteras (*Anal. Fis. Quim.*, 1940, **36**, 354—359).—The derivative, m.p. 112—115°, of García Banus *et al.* (A., 1922, i, 333) is *p*-$C_6H_4Ph{\cdot}NMe{\cdot}NO$ (m.p. 115—116°) (with HNO_2 gives the 3-NO_2-derivative); 3-nitro-4-dimethylaminodiphenyl (I), m.p. 70—71°, is also formed. *p*-$C_6H_4Ph{\cdot}NMe_2$ or (I) with AcOH–HNO_2 yields 3 : 5-*dinitro-*, m.p. 104—105°, reduced by Na_2S to 3-nitro-5-amino- [*hydrochloride*, m.p. 175—180° (decomp.)], by $SnCl_2$ to 3 : 5-*diamino*-4-*dimethylamino-*, m.p. 113—115° (oxidised by CrO_3 to BzOH), and converted by HNO_2 into 3 : 5-dinitro-4-nitrosomethylamino-diphenyl, m.p. 121—122°. The nitration of bases by HNO_2 is considered to take place through a quinonoid form, which has been isolated in the case of (*p*-$NMe_2{\cdot}C_6H_4)_2$, and subsequent nitration. Quinol with $C_6H_{11}{\cdot}O{\cdot}NO$ gives quinhydrone and benzoquinone. F. R. G.

Intramolecular transformations among completely substituted benziminophenylthiocarbamides and thiobenzoylguanidines. H. Rivier and M. Langer (*Helv. Chim. Acta*, 1943, **26**, 1722—1740).—PhCS·NPh·C(:NPh)·NPhR is converted by heat into NPh:CPh·NPh·CS·NPhR when R = Et. Change occurs in the reverse direction when R = Me. The mechanism of the reactions is discussed. Carbodiphenylimide (I) (trimeric) is converted by an

equimol. quantity of NHPhAlk at room temp. into 2-*methylanilino*-1 : 2 : 3 : 4 : 5 : 6-*hexaphenyldihydro*isomelamine, NPh<C(:NPh)·NPh / C(:NPh)·NPh>C(NHPh)·NPhMe, m.p. 144—145°, and the corresponding *Et* compound, m.p. 149—150°. At ~110° the corresponding products are NN′N″-*triphenyl*-N-*methyl*- (**II**), m.p. 128—129° (*hydrochloride*, m.p. 216—217°), and -N-*ethyl*-, m.p. 89—90° (*hydrochloride*, m.p. 205—206°), -*guanidine*. Nascent (**I**) and NHPhMe give an isomeride (**III**), m.p. 115—116° (rapid), ~127° (slow heating) (hydrochloride, m.p. 205—206°), of (**II**). (**II**) or (**III**) is transformed by BzCl in alkali or $CHCl_3$–C_5H_5N into N″-*benzoyl*-NN′N″-*triphenyl*-N-*methylguanidine*, m.p. 194—195°; the corresponding *Et* compound has m.p. 109—110°. PhCSCl and (**II**) (Schotten–Baumann) give N″-*thiobenzoyl*-NN′N″-*triphenyl*-N-*methylguanidine* (**IV**), m.p. 182—183° (*hydrochloride*, decomp. ~160°; picrate, m.p. 188—189°), also obtained from chlorodiphenylmethylamidine and PhCS·NHPh in $CHCl_3$ containing C_5H_5N. N″-*Thiobenzoyl*-NN′N″-*triphenyl*-N-*ethylguanidine* (**V**), m.p. 130·5—131°, and its hydrochloride are described. Since either base is readily regenerated from its hydrochloride there is no transformation under the influence of HCl under these conditions. Addition of NPh:CPhCl in $CHCl_3$ (free from EtOH) to a solution of NPh:C(SH)·NPhMe in $CHCl_3$ containing C_5H_5N at room temp. gives N′-N-*phenylbenzimino*-N′N″-*diphenyl*-N″-*methylthiocarbamide* (**VI**) (+C_6H_6 or +Et_2O), m.p. 96—98°; the corresponding *Et* compound (**VII**) has m.p. 131—132° (also +$1C_6H_6$, m.p. 89—91°). In the initial absence of C_5H_5N these reactants give isomerides of (**VI**) and (**VII**) (as red hydrochlorides); C_5H_5N then gives (**IV**) and (**VII**) [or (NPh:CPh)$_2$S] respectively. NPh:CCl·NPhMe and NPh:CPh·SNa give (**VI**). *Chloro*-NN′-*diphenyl*-N-*ethylamidine* b.p. 196—200°/10 mm., m.p. 58—59°, under similar conditions affords (**VII**). (**VI**) is also obtained from NPh:CPh·NHPh and NPhMe·CSCl in $CHCl_3$ (free from EtOH) at 30—35°; with the crude chloride in boiling $CHCl_3$ the product is triphenyldimethyldithiobiuret, m.p. 204—205°. (**VII**) is obtained analogously from NPhEt·CSCl. (**VI**) and (**VII**) afford yellow hydrochlorides from which the bases are readily regenerated by C_5H_5N, showing that under the experimental conditions there is no transformation under the influence of HCl. (**IV**) is unchanged by boiling C_6H_6 whereas under these conditions (**V**) is partly converted into (**VII**). (**VI**) remains unchanged in boiling C_6H_6 whereas at 180—200° it is converted into (**IV**). N′-N-*Phenylbenzimino*-N′-*phenylthiocarbamyl chloride*, m.p. 112—113°, is prepared from NPh:CPh·NHPh and $CSCl_2$ in $CHCl_3$. M.p. are corr. H. W.

anti-α-**Hydroxylamino**-γ-**oximino**-α$_2$-**di**-*p*-**amsyl**-Δ$^\delta$-**pentene, m.p. 156—157° (corr.).**—See C., 1944, 64.

Synthesis of chloro-ortho-esters of silicic acid. J. N. Volnov and A. Mischelevitsch (*J. Gen. Chem. Russ.*, 1943, **13**, 213—216).—The following esters were obtained from $SiCl_4$ and the appropriate OH-compound in Et_2O: *trichlorothymoxysilan*, b.p. 122—124°/23 mm., *dichlorodithymoxysilan*, b.p. 195—200°/3 mm., *chlorotrithymoxysilan*, b.p. 251—255°/7—8 mm. *trichlorocarvacryloxysilan*, b.p. 108—111°/4 mm., and *trichloro*-o-*anisyloxysilan*, b.p. 134—136°/30 mm. R. T.

Dipole moments of friedelin, cerin, isomerides of friedelinol, and isomerides of γ-(α-**naphthyl**)-α-**chloro**-Δ$^\alpha$-**propene.**—See A., 1944, I, 1.

Syntheses of 2 : 4 : 6-trialkylresorcinols from products of the Nidhone process. I. 2 : 4 : 6-Triethylresorcinol. S. D. Limaye (*Rasāyanam*, 1943, **1**, 246—250).—2 : 1 : 3-$C_6H_3Et(OH)_2$ gives (Ac_2O–NaOAc at 155—160°) its *diacetate*, m.p. 70—71°, which with $AlCl_3$ at 150° yields 4 : 6-*diacetyl*-2-*ethylresorcinol*, m.p. 110°, reduced (Clemmensen) to 2 : 4 : 6-*triethylresorcinol* (**I**), m.p. 85°. 2 : 4 : 1 : 3-$C_6H_2Et_2(OH)_2$ with AcOH–ZnCl$_2$ at 140° gives 6-*acetyl*-2 : 4-*diethylresorcinol*, m.p. 115°, giving (**I**) on reduction. 4 : 6 : 1 : 3-$C_6H_2Ac_2(OH)_2$ with AcCl and $AlCl_3$ at 110° gives 2 : 4 : 6-*triacetylresorcinol*, m.p. 136°, also reduced to (**I**). D. G.

Migration of radicals during a Grignard reaction. αα-**Di**-*p*-**hydroxyphenyl**-ββ-**diethylethylene.** Z. Foldi and I. Demjen (*Ber.*, 1941, **74**, [*B*], 930—934).—Anisoin and $SOCl_2$ at 50° give *chlorodeoxyanisoin* (**I**), m.p. 80—82°, which with MgEtBr gives (*p*-OMe·C_6H_4)$_2$CH·CEt_2·OH (**II**), m.p. 84—85°, b.p. 164—167°/~0·01 mm., converted by $POCl_3$ alone at room temp. into (*p*-OMe·C_6H_4)$_2$C:CEt_2 (**III**), m.p. 90—92°, or by $POCl_3$ in PhMe at 100° into (*p*-OMe·C_6H_4·CEt:)$_2$, m.p. 121—123° (cf. Peteri, A., 1940, II, 306; von Wessely *et al.*, *Monatsh.*, 1940, **73**, 132). Structures are proved as follows. CrO_3–AcOH at room temp. and then 100° oxidises (**I**) to anisil; with MgMeI, (**II**) gives 80—85% of CH_4, and with CrO_3–AcOH gives (*p*-OMe·C_6H_4)$_2$CO; KOH–EtOH at 200° converts (**III**) into (*p*-OH·C_6H_4)$_2$C:CEt_2, m.p. 170—173°, and H_2–Pd–C in EtOH gives (*p*-OMe·C_6H_4)$_2$CH·$CHEt_2$, b.p. 115—124°/~0·01 mm. With a little H_2SO_4 and distillation at ~0·01 mm., (**II**) yields (**III**). PBr_3 converts (**II**) into an oily bromide, which with boiling KOH–EtOH yields (**III**). R. S. C.

Natural stilbenes. III. Synthesis of resveratrole. E. Spath and K. Kromp. **IV. Synthesis of pinosylvin.** E. Spath and F. Liebherr. **V. Synthesis of pinosylvin monomethyl ether.** E. Spath and K. Kromp (*Ber.*, 1941, **74**, [*B*], 867—869, 869—872, 1424—1428).—III. 3 : 5 : 1-$(OH)_2C_6H_3$·CHO (**I**) and *p*-OH·C_6H_4·CO_2Na in Ac_2O at 160° give, after keeping in aq. NaOH–N_2 at room temp., 3 : 5-*dihydroxy*-α-p-*hydroxyphenylcinnamic acid* (46%), m.p. 284—286° (decomp.), decarboxylated to resveratrole (Takaoka, A., 1940, II, 328) (CH_2N_2 gives the Me_3 ether = pterostilbene) by Cu-bronze in quinoline at 220° (4 min.).

IV. 3 : 5 : 1-$(OAc)_2C_6H_3$·CO_2H and $SOCl_2$ at 60—70° give the acid *chloride*, m.p. 89·5—90°, converted by H_2–Pd–$BaSO_4$ in xylene at 160° into (**I**), m.p. 161—162° (decomp.) (lit., 145—146°) (*diacetate*, m.p. 53·5—54·5°). $CH_2Ph·CO_2Na$ (**II**) and (**I**) in Ac_2O at 100° and then 160° give 3 : 5-*diacetoxy*-α-*phenylcinnamic acid* (46%), m.p. 197·5—198·5°, converted by Cu-bronze in quinoline at 260° and then 240° into an oil which with boiling 5% aq. NaOH–N_2 gives pinosylvin.

V. 3 : 5 : 1-$(OH)_2C_6H_3$·CO_2Me and Me_2SO_4 in MeOH–NaOMe at 20° and then the b.p. give 3-*hydroxy*-5-*methoxybenzoic acid* (36%), m.p. 203—204° (and a small amount of the Me_2 ether ester), converted by boiling AcCl into the *acetate*, m.p. 151·5—152·5°, which with $SOCl_2$ at 75° gives 3-*acetoxy*-5-*methoxybenzoyl chloride*. H_2–Pd–$BaSO_4$ in xylene at 160° then gives 3 : 5 : 1-OH·C_6H_3(OMe)·CHO, m.p. 130—131°, which with (**II**) in Ac_2O at 160° and then aq. KOH–N_2 at 20° gives 3-*hydroxy*-5-*methoxy*-α-*phenylcinnamic acid* (**III**), m.p. 200—201°, and a small amount of an isomeric *acid* (**IV**), m.p. 181—182°. With Cu-bronze in quinoline at 240° and then 220°, (**III**) gives an oil, isomerised by short heating at 350°/vac. (not other methods) into pinosylvin Me ether (67% yield), m.p. 121·5—122°, which is obtained directly by decarboxylation of (**IV**). R. S. C.

Structure of hydroxyazo-dyes according to their absorption spectra. Spectroscopic analysis of acyloxyazo-compounds. P. Ramart-Lucas (*Compt. rend.*, 1942, **215**, 468—470).—Spectra of (:NPh)$_2$. *p*-OAc·C_6H_4·N_2Ph, *p*-NPhAc·N:C_6H_4:O, and 4 : 1 : 3-OAc·C_6H_3Me·N_2Ph are recorded; the spectrum of the *O*-Ac derivatives is very close to that of (:NPh)$_2$. The structure of acyloxyazo-compound is therefore determinable from their spectra. H. W.

Action of montmorillonite clays on vitamin-*A*. Mesomerism in the carotenoid group. P. Meunier (*Compt. rend.*, 1942, **215**, 470—473).—Montmorillonite clays become blue by the adsorption of vitamin-*A* from non-polar solvents (C_6H_6, light petroleum, *cyclo*hexane, and even $CHCl_3$). Other clays behave similarly after treatment with HCl or H_2SO_4. The colour is very persistent, particularly if the clay is soaked in the solvent. It can easily be removed by a trace of a polar solvent (EtOH, $COMe_2$, Et_2O). If the latter is removed and a polar solvent used again, the blue colour reappears. It is considered that mesomerism between the ψ-quinonoid and ψ-benzenoid forms is caused by the reaction of widely differing reagents, all of which have incomplete octets, on carotenoids in non-polar media. A trace of polar solvent causes the disappearance of mesomerism (and the colour reaction in consequence) by a mutual attraction of the dipoles; the mol. -*A* is detached in one of its forms. The colour with the clays is thus brought into line with that given by $SbCl_3$. H. W.

Contact synthesis of *o*-methylbenzyl alcohol from crotonaldehyde and ethyl alcohol. J. A. Gorin and K. N. Tscharskaja (*J. Gen. Chem. Russ.*, 1943, **13**, 131—135).—A mixture of CHMe:CH·CHO and EtOH passed over the dehydrating component of Lebedev's catalyst (A., 1934, 168) at 350° gives *o*-C_6H_4Me·CH_2·OH in 5% yield. R. T.

Phenol–formaldehyde resins. II. Quinonemethide as intermediate product in the hardening of phenol resins. V. Reactions of *p*-hydroxymethyl groups during hardening. VI. Oxido-reduction processes during heating of polymeric quinonemethides. K. Hultzsch (*Ber.*, 1941, **74**, [*B*], 898—904, 1533—1538, 1539—1543).—II. Heating 2 : 3 : 5 : 1-OH·$C_6H_2Me_2$·CH_2·OH (**I**) at 175° in CO$_2$ gives H_2O, an oil, and a resin containing a di- or tri-meride, m.p. 200° (**II**), of 1 : 3 : 5 : 2-CH_2:$C_6H_2Me_2$:O and much (2 : 3 : 5 : 1-OH·$C_6H_2Me_2$·CH_2)$_2$O (**III**), m.p. 100° (*diacetate*, m.p. 85·5°). At 190—200° (**III**) gives (**II**) and at 225° gives (2 : 3 : 5 : 1-OH·$C_6H_2Me_2$)$_2$$CH_2$ (**IV**) (does not condense with paraformaldehyde at 200—240°). Heating (**II**) to 240° in CO_2 causes darkening and formation of (2 : 3 : 5 : 1-OH·$C_6H_2Me_2$·CH_2)$_2$ (**V**), m.p. 168° (diacetate, m.p. 124°; Br_4-derivative, m.p. 258°), and a tetracyclic resin, but no H_2O or CH_2O. Heating (**I**) rapidly to 235° in CO$_2$ gives H_2O, CH_2O, (**IV**), (**V**), and 2 : 3 : 5 : 1-OH·$C_6H_2Me_2$·CHO. Quinonemethides are considered to be intermediates in the hardening of (**I**) etc., reacting by disproportionation and diene addition.

V. Hardening of 4 : 3 : 5 : 1-OH·$C_6H_2Me_2$·CH_2·OH (**VI**) proceeds similarly to that of (**I**) by way of the quinonemethide, but is slower and requires a higher temp.; it is, however, very rapid if other mols. have free *p*-positions. 68% of (**VI**), m.p. 105°, with very little (4 : 3 : 5 : 1-OH·$C_6H_2Me_2$)$_2$$CH_2$ (**VII**) is obtained from 1 mol. each of 2 : 6 : 1-$C_6H_3Me_2$·OH (**VIII**), 30% CH_2O, and 10% NaOH in the cold. (**VI**) is partly unchanged by distillation at 1 mm., but ~50% is resinified, giving, *inter alia*, (**VII**), m.p. 175°. Heating (**VI**) at 230—240° in CO$_2$ gives H_2O, CH_2O (a little), 4 : 3 : 5 : 1-OH·$C_6H_2Me_2$·CHO, mesitol (a trace), (4 : 3 : 5 : 1-OH·$C_6H_2Me_2$·CH_2)$_2$, (4 : 3 : 5 : 1-OH·$C_6H_2Me_2$·CH:)$_2$ (**IX**), an *isomeride*, m.p. 224—226°

[gives the known (4 : 3 : 5 : 1-OH·$C_6H_2Me_2$·$CHBr)_2$, m.p. 178—186° (decomp.)], of (**IX**), and a resin (mol. wt. 584) (cf. Adler *et al.*, A., 1943, II, 130).

VI. Hardening of *o*-hydroxybenzyl alcohols containing no free *o*- or *p*-position is held to proceed entirely by way of *o*-quinonemethides, which dimerise to coumaran derivatives and thence, by oxidation and reduction, give all the products hitherto isolated. Similarly *p*-hydroxybenzyl alcohols give *p*-quinonemethides, which dimerise to stilbene derivatives, whence all isolated products are derived by oxidation and reduction. Isolation of mesitol after heating (**I**) is described. 2-Hydroxy-5-*cyclo*hexyl-3-methylbenzyl alcohol gives 4-cyclo*hexyl*-2 : 6-*dimethylphenol*, m.p. 78—79°, also obtained from (**VIII**) by *cyclo*hexanol and 72% H_2SO_4 at 60—70°; 2 : 3 : 5 : 1-OH·C_6H_2MeBu^t·CH_2·OH gives 2 : 6-*dimethyl*-4-tert.-*butylphenol*, m.p. 81—82°, also obtained from (**VIII**) by Bu^{t}OH and 72% H_2SO_4 at 60—70°. R. S. C.

Cyclic compounds containing sulphur.—See A., 1944, II, 154.

9 : 10-Dialkyl-9 : 10-dihydrophenanthrenediols and related compounds. E. J. H. Chu and Z. I. Shen (*J. Chinese Chem. Soc.*, 1943, 10, 116—118).—Phenanthraquinone and MgAlkBr give 9 : 10-*di*-n-*hexyl*- (64%), m.p. 93·3—94·3°, -*di*-n-*heptyl*- (80%), m.p. 78·6—78·8°, and -*di*-n-*octyl*-9 : 10-*dihydrophenanthrene*-9 : 10-*diol* (69%), m.p. 92·3—93·2°, which yield oils on attempted rearrangement. The 9 : 10-Bu^n_2 analogue (78%), m.p. 134·5—136·5°, is rearranged by boiling AcOH–I to 10 : 10-*di*-n-*butyl*-9-*phenanthrone* (94%), m.p. 71·8—72·8°, reduced (Clemmensen) to 9 : 9-*di*-n-*butyl*-9 : 10-*dihydrophenanthrene* (10%), m.p. 76° (cf. Bachmann *et al.*, A., 1932, 745). A. T. P.

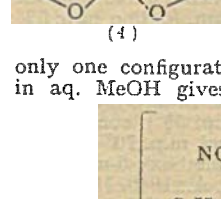
Mercapturic acids. IV. Synthesis of *p*-fluorophenyl-*l*-cysteine and its conversion into *p*-fluorophenylmercapturic acid *in vitro* and *in vivo*. S. H. Zbarsky and L. Young (*J. Biol. Chem.*, 1944, **152**, 599—602).—Cysteine Cu^{II} mercaptide (A., 1944, II, 76) and *p*-C_6H_4F·N_2HSO_4 at 0°, then at 60—70°, afford, after purification with Sn–aq. HCl at 100° (bath), p-*fluorophenyl*-l-*cysteine* (**I**), decomp. 180—183°, $[\alpha]_D^{22}$ +13° in 0·1N-NaOH. Successive treatment of (**I**) with 0·1N-NaOH and Ac_2O at 0° gives p-*fluorophenylmercapturic acid*, m.p. 158—159°, $[\alpha]_D$ −20° in EtOH, which is isolated (14—15% conversion) from the urine of rats fed on a diet containing (**I**). A. T. P.

1 : 1-Diphenylindane and its derivatives. 1 : 1-Diphenyl-3-indanyl- and -3-indenyl-acetic acids. P. E. Gagnon, L. Gravel, and L. P. Amiot (*Canad. J. Res.*, 1944, **22**, B, 32—44).—1 : 1-Diphenylindane (**I**) (improved prep.) with Br (1 mol.) in boiling CS_2 gives the 3-*Br*-derivative (**II**), m.p. 87—88°, converted by MeOH, EtOH, piperidine, *p*-toluidine, and NH_2Ph into 3-*methoxy*- (**III**), m.p. 101—102°, 3-*ethoxy*-, m.p. 70—71°, 3-*piperidino*-, m.p. 108—109° (*hydrochloride*, m.p. 253—255°), 3-p-*toluidino*-, m.p. 124—125° (*hydrochloride*, m.p. 218—219°), and 3-*anilino*-1 : 1-*diphenylindane*, m.p. 125—126° (*hydrochloride*, m.p. 213—214°), respectively. With aq. KOH or K_2CO_3, (**II**) gives 1 : 1-diphenylindene (**IV**), m.p. 90—91°, and a little *di*-(1 : 1-*diphenyl*-3-*indanyl*) *ether*, m.p. 192—195°, while (**III**) and boiling 48% HBr yields (**IV**). (**II**) with CHNa$(CO_2Et)_2$ in boiling PhMe gives *Et* 1 : 1-*diphenyl*-3-*indanylmalonate*, b.p. 268°/1 mm.; the *malonic acid*, m.p. 160° (*Ag* salt; *di*-p-*nitrobenzyl* ester, m.p. 73—75°), at 170—180° gives 1 : 1-*diphenyl*-3-*indanylacetic acid* (**V**), m.p. 173—174° [*Ag* salt; p-*nitrobenzyl* ester, m.p. 172—173°; *amide* (**VI**), m.p. 181—182°; *anilide*, m.p. 171—172°]. Boiling $SOCl_2$ and (**VI**) yield 1 : 1-*diphenyl*-3-*indanylacetonitrile*, m.p. 120—121°, reduced (Na, EtOH) to β-1 : 1-*diphenyl*-3-*indanylethylamine* (*hydrochloride*, m.p. 180—185°). (**VI**) and Et_2O–EtOH–HCl give a *hydrochloride*, m.p. 191—192°. 3 : 3-Diphenylindanone with CH_2Br·CO_2Et (Reformatsky) gives *Et* 3-*hydroxy*-1 : 1-*diphenyl*-3-*indanylacetate*, m.p. 93—94°, dehydrated (HCl in PhMe) to *Et* 1 : 1-*diphenyl*-3-*indenylacetate* (**VII**), m.p. 80—81° [free *acid* (**VIII**), m.p. 178—179° (*Ag* salt; p-*nitrobenzyl* ester, m.p. 142—143°)]. Reduction (H_2, PtO_2, AcOH) of (**VIII**) [or (**VII**) and subsequent hydrolysis] gives (**V**). D. G.

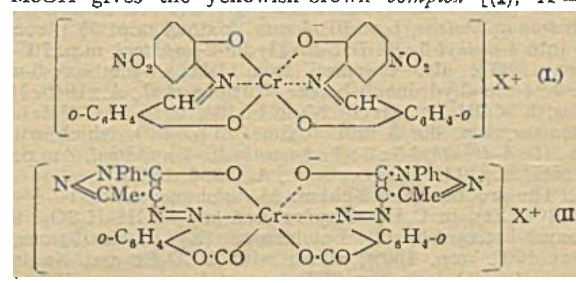
αα′α′-Ditetramethyleneadipic [ethylene-αβ-bis*cyclo*pentane-1 : 1′-dicarboxylic] acid. Ring-contraction by oxidation. C. Mannich (*Ber.*, 1941, **74**, [*B*], 1007—1014).—*cyclo*Pentane*spiro*-1′ : 2-*cyclo*pentanone*spiro*-3 : 2 -*cyclo*hexanone (A., 1943, II, 373) with 30% H_2O_2 in AcOH gives exothermally (cooling) αα-α α′-*ditetramethyleneadipic acid* (**I**) (87%), m.p. 220°, sublimes 205—210°, the structure of which follows from proof that it is symmetrical (below) and from the facts that it (i) resists dehydrogenation by Pt–asbestos at 300—500°, Br at 165° (partial decomp.; complete at 195°), or Se at 300° [gives a small amount of 1-β-cyclo*pentylethyl*cyclo*pentane*-1-*carboxylic acid*, m.p. 35—36° (amorphous *Ag* salt), and CO_2], (ii) is partly decomposed but not decarboxylated by Cu-bronze in acridine–N_2 at 300°, (iii) is 50% decomposed and 50% unchanged by Br and red P at 100°, (iv) does not undergo condensation to a ketone, and (v) in boiling Ac_2O gives a dimeric *anhydride* (**II**), m.p. 187° [hydrolysed to (**I**) by alkali but unaffected by boiling MeOH]. With boiling $SOCl_2$–C_6H_6 and then NH_3–MeOH at 0°, (**I**) gives the *diamide* (77%), m.p. 245—246°. With CH_2:CH·CH_2·NH_2 (**III**) in C_5H_5 at 45°, (**II**) gives the *mono*- (**IV**) (~50%), dimorphic, m.p. 84° (resolidifies, remelts 103°) and 103°, and the *di-allylamide* (**V**), m.p. 205°. The *mono*- (**VI**) (~50%), m.p. 93°, and *di*-n-*propylamide* (**VII**), m.p. 218°, are similarly prepared. The N-*propyl*-N′-*allyldiamide*, m.p. 213°, is prepared from (**IV**) by $SOCl_2$ at 40° and then NH_2Pr^n–EtOH at 0° or from (**VI**) by $SOCl_2$ and then (**III**); a mixture of (**V**) and (**VII**) shows a sharp m.p. (214—215°), so that this proof of symmetry is invalid. Me_2SO_4–NaOH converts (**I**) into the *Me*$_2$ ester (**VIII**), m.p. 88°; HCl–EtOH at room temp. gives the *Et*$_2$ ester, b.p. 189—190°/4 mm. The Na$_2$ salt of (**I**) with CH_2PhCl in boiling MeOH gives the (*CH*$_2$*Ph*)$_2$ ester (**IX**), m.p. 91°. Boiling KOH–90% MeOH converts (**VIII**) into the *Me H* ester (**X**) (50%), m.p. 85°, which with boiling $SOCl_2$–C_6H_6 and then NH_4Ph–$COMe_2$ gives *Me aaa a -ditetramethyleneadipanilate*, m.p. 115° [*anilic acid* (**XI**), m.p. 163°]. With Na and a little H_2O in CH_2Ph·OH at 100°, (**IX**) gives the *CH*$_2$*Ph H* ester, m.p. 105° [also obtained, less well, from (**II**) by CH_2Ph·OH] [*anilide*, m.p. 96°, gives (**XI**) by mild hydrolysis], which with CH_2N_2 gives the *CH*$_2$*Ph Me* ester (**XII**), m.p. 39°. (**XII**) is also obtained from the K salt of (**X**) by CH_2PhCl in boiling MeOH and is converted into (**X**) by H_2–Pd–C in MeOH. The sparingly sol. Ca salt of (**I**) at 470—550° gives *cyclo*pentane-*spiro*-1 : 2′-*cyclo*pentanone, b.p. ~165°/13 mm. (*semicarbazone*, m.p. 211°, absorbs no H_2 in presence of Pd–C). R. S. C.

Aceconitic acid. C. Grundmann (*Annalen*, 1943, **555**, 77—80).—Aceconitic acid, m.p. 220—221° (corr.) [Me_3 ester, m.p. 56—57° (corr.); very sparingly sol. *Ba* salt], obtained by Baeyer (*Annalen*, 1865, **135**, 308) by the action of Na on CH_2Br·CO_2Et, is identified as *trans-cyclo*propane-1 : 2 : 3-tricarboxylic acid. Lower yields are obtained from CH_2Cl·CO_2Et. H. W.

Optically active chromium lakes. P. Pfeiffer and S. Saure (*Ber.*, 1941, **74**, [*B*], 935—941).—For hexaco-valent, tetrahedral compounds (*A*), there are 6 optically active *cis*- and 4 optically active *trans*-isomerides, plus 5 corresponding racemates. However, if R = R′, there are only two active (+ its racemate) forms and one, inactive *trans*-form. The Cr compounds described below were obtained in only one configuration. The Na salt [(**I**), X = Na] with H_2SO_4 in aq. MeOH gives the yellowish-brown *complex* [(**I**), X = H],



(*A*)



which gives no cryst. quinine salt but with CHPhMe·NH_2 gives the *dl*-base *dl*-acid *salt* and with the *d*-base gives a *salt*, $[M]_D$ −2196° in 50% EtOH, whence dil. H_2SO_4 yields the l-*complex* [(**I**), X = H], α ~0 in 50% EtOH, $[M]_D$ −2196° as Na salt in 50% EtOH. The Na salt [(**II**), X = Na] gives similarly the *substance* [(**II**), X = H] which with strychnine yields *salts*, $[M]_D$ +820° and −1438°, and thence *substances* [(**II**), X = H], $[M]_D$ (as Na salt) +1109° and −693°, respectively, in 50% EtOH. R. S. C.

Preparation of retinene *in vitro*.—See A., 1943, III, 405.

Alkylation by olefines in presence of aluminium chloride. II. S. I. Lurie and A. J. Golovatscheva (*J. Gen. Chem. Russ.*, 1943, **13**, 195—201).—Butylation of COMeR (R = Ph, 2 : 4-$C_6H_3Me_2$, 2 : 5- and 2(4) : 4(2)-OMe·C_6H_3Me) by means of CH_2:CMe_2 in CS_2 in presence of $AlCl_3$ does not take place, suggesting that the CO group inactivates the mol. R. T.

Ring enlargement in cyclanes. Methyl*cyclo*pentane, *cyclo*heptane, and indane series. (Mlle.) B. Tchoubar (*Compt. rend.*, 1942, **215**, 224—225).—2-Methyl*cyclo*pentanone is converted into its *cyanohydrin*, b.p. 134—135°/35 mm., which is hydrogenated (PtO_2) to 2-*methyl*-1-*aminomethyl*cyclo*pentanol*, b.p. 105°/15 mm. (*hydrochloride*, m.p. 157°). This is deaminated ($NaNO_2$–dil. AcOH) exclusively to 3-methyl*cyclo*hexanone (semicarbazone, m.p. 178°). Rupture of the ring occurs only between $C_{(1)}$ and $C_{(2)}$. 3-*Methyl*-cyclo*pentanone cyanohydrin*, b.p. 122—124°/19 mm., is hydrogenated to 3-*methyl*-1-*aminomethyl*cyclo*pentanol*, b.p. 115°/20 mm., deaminated to 3- and 4-methyl*cyclo*hexanone (semicarbazones, m.p. 178° and 198°, respectively), fission occurring mainly between C·C on the substituted side of the ring. cyclo*Heptanone cyanohydrin*, b.p. 138—139°/15 mm., affords 1-*aminomethyl*cyclo*heptanol*, b.p. 14° (?)/18 mm. (*hydrochloride*, m.p. 185°), deaminated to *cyclo*octanone, b.p. 90°/12 mm. (semicarbazone, m.p. 164—165°). 2-Indanone is converted through the H sulphite into the *cyanohydrin*, m.p. 121°, and thence into the NH_2-alcohol, which is deaminated directly to 2-keto-1 : 2 : 3 : 4-tetrahydronaphthalene (semicarbazone, m.p. 215°). H. W.

Syntheses in the santonin series. I. 4-Alkyl-$\Delta^{2:5}$-*cyclo*hexadienones. II. 2-Keto-1 : 10-dimethyl-$\Delta^{1(9):3}$-hexahydronaphthalene. III. Santonin. (Miss) K. Paranjape, N. L. Phalnikar, B. V. Bhide, and K. S. Nargund (*Rasāyanam*, 1943, **1**, 233—237, 237—243, 243—245).—I. Et Δ^{α}-nonenoate, HCO_2Et, and Na in Et_2O give *Et γ-formyl-*Δ^{α}*-nonenoate* (**I**), b.p. 120°/8 mm. (*p*-nitrophenylhydrazone, m.p. 113°), oxidised (cold aq. $KMnO_4$ + $MgSO_4$) to *n*-amylmalonic acid (**II**). (**I**) with $CH_2(CO_2H)_2$ in C_5H_5N–piperidine at 100° (bath) gives *Et H γ-n-amyl-*$\Delta^{\alpha\delta}$*-pentadiene-*$\alpha\varepsilon$*-dicarboxylate*, b.p. 130°/4 mm., and thence (alkali) the free *acid* (**III**). With $Ba(OH)_2$ at 180° (**III**) gives 4-n-*amyl*-$\Delta^{\cdot:5}$-cyclo*hexadienone*, b.p. 194°/713 mm. (*oxime*, m.p. 48°; *p-nitrophenylhydrazone*, m.p. 99°), oxidised to (**II**) and converted by conc. HCl at room temp. (21 days) into *p-n*-amylphenol. Similarly Et hexenoate gives *Et γ-formyl-*Δ^{α}*-hexenoate*, b.p. 65°/8 mm. (p-*nitrophenylhydrazone*, m.p. 71°), *Et H γ-ethyl-*$\Delta^{\alpha\delta}$*-pentadiene-*$\alpha\varepsilon$*-dicarboxylate*, b.p. 80°/8 mm. (free *acid*), and 4-*ethyl*-$\Delta^{2\cdot5}$-cyclo*hexadienone* (**IV**), b.p. 160°/713 mm. (p-*nitrophenylhydrazone*, m.p. 83°). (**IV**) with fuming HCl followed by Br gives 4 : 2 : 3 : 6 : 1-C_6HEtBr_3·OH, m.p. 57—58°.

II. 2-Formyl*cyclo*hexanone (**V**), $CH_2(CO_2H)_2$, and C_5H_5N–piperidine give *β*-2-*keto*cyclo*hexylacrylic acid*, two forms, probably geometric isomerides, b.p. 120°/20 mm. (**VI**) (*semicarbazone*, m.p. 185°; *Me* ester, b.p. 100°/40 mm., and its *semicarbazone*, m.p. 195°), and b.p. 200 / 20 mm. (**VII**) (*semicarbazone*, m.p. 225°; *Me* ester, b.p. 210°/40 mm., and its *semicarbazone*, m.p. 225°). Oxidation ($KMnO_4$) of (**VI**) or (**VII**) gives *cyclo*hexanone-2-carboxylic acid. The Me ester of (**VI**) with $CH_2Br{\cdot}CO_2Et$ gives (Reformatsky) a OH-ester, b.p. 144°/30 mm.; hydrolysis (EtOH–KOH) and dehydration (Ac_2O) gives (poor yield) *β-2-carboxymethylene*cyclo*hexylacrylic acid*, m.p. 86°, which gives a trace of (?) (**VIII**) (below) on distillation with $Ba(OH)_2$. (**V**) with $COMe_2$ and NaOEt in EtOH gives 2-*keto*-$\Delta^{1(9)\cdot3}$-*hexahydronaphthalene* (**VIII**), b.p. 105°/25 mm. (semicarbazone, m.p. 115°; oxime, m.p. 72°). With boiling conc. HCl (**VIII**) gives 5 : 6 : 7 : 8-tetrahydro-2-naphthol, m.p. 62°. (**V**) with COMeEt gives 2-*keto*-1-*methyl*-$\Delta^{1(9):3}$-*hexahydronaphthalene*, b.p. 85°/5 mm. (oxime, m.p. 52°; *p*-nitrophenylhydrazone, m.p. 92°), which with HCl gives 1-*methyl*-5 : 6 : 7 : 8-*tetrahydro*-2-*naphthol*, m.p. 78° (benzoate, m.p. 91°). (**V**) (Na salt) with MeI in C_6H_6 at 60° gives 2-formyl-2-methyl*cyclo*hexanone (**IX**), which with $COMe_2$ gives 2-*keto*-10-*methyl*-$\Delta^{1(9):3}$-*hexahydronaphthalene*, b.p. 70°/5 mm. (oxime, m.p. 55°), converted (HCl) into 4-*methyl*-5 : 6 : 7 : 8-*tetrahydro*-2-*naphthol*, m.p. 70° (*benzoate*, m.p. 89°), also prepared from 1-keto-7-methoxy-5-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene (Ruzicka *et al.*, A., 1940, II, 184). (**IX**) with COMeEt gives 2-*keto*-1 : 10-*dimethyl*-$\Delta^{1(9):3}$-*hexahydronaphthalene*, b.p. 60°/5 mm. (oxime, m.p. 48°), which with HCl yields 1 : 4-*dimethyl*-5 : 6 : 7 : 8-*tetrahydro*-2-*naphthol*, m.p. 108° (benzoate, m.p. 119°) (Fieser *et al.*, A., 1936, 1503).

III. The product from 3-chloro-Δ^2-*cyclo*hexenone and $CMeNa(CO_2Et)_2$ in C_6H_6 is hydrolysed (aq. EtOH–H_2SO_4) to α-(2-hydroxy-3-keto*cyclo*hexyl)propiolactone (**X**) (*semicarbazone*, loses H_2O at 100°, m.p. 150°), which with HCO_2Et and Na in Et_2O gives the 4-CHO-derivative (**XI**) (*semicarbazone*, m.p. 199°) of (**X**). The Na derivative of (**XI**) with MeI in C_6H_6 at 60° affords the 4-Me derivative of (**XI**), which with COMeEt and NaOEt gives santonin (**XII**), m.p. 171° (semicarbazone, m.p. 203°), identical (mixed m.p.) with natural (**XII**). The synthetic (**XII**) was optically active (lævorotatory); this is claimed to be the first example of an abs. asymmetric synthesis. D. G.

Syntheses in the naphthalene group. IV. Cyclisation of phenylbenzylpyrotartaric [α-(α′β′-diphenylethyl)succinic] acid. W. Borsche and F. Sinn (*Annalen*, 1943, **555**, 70—77; cf. A., 1937, II, 18).—Cyclisation of α-(α′β′-diphenylvinyl)succinic acid (**I**) [prep. from $COPh{\cdot}CH_2Ph$ and $(CH_2{\cdot}CO_2Et)_2$ described] gives mixtures of compounds from which only very small amounts of individuals can be isolated. (**I**) is reduced by Na–Hg at 100° to a mixture (**II**) of isomerides (racemates of the potentially active and *meso*-forms) from which α-(α′β′-*diphenylethyl*)*succinic acid* (**III**), m.p. 186—187°, is readily isolated. It is also obtained by hydrogenation (Pd–C in EtOH) of the Et_2 ester of (**I**) and hydrolysis of the product. (**III**) gives (CH_2N_2) a Me_2 ester and is converted by boiling AcCl into an *anhydride* (**IV**), m.p. 102—103°, re-converted by KOH–MeOH into (**III**). Treatment of (**III**) with NaOAc and boiling Ac_2O affords predominatingly an *anhydride* (**V**), m.p. 133—134°, hydrolysed (KOH–MeOH) to iso-α′β′-*diphenylethylsuccinic acid* (**VI**), m.p. 150—151°, or (+1 C_6H_6), m.p. 96° (decomp.) and 151° after resolidification. (**VI**) and CH_2N_2 give a *Me*$_2$ ester, m.p. 114·5—115·5°, also obtained from (**V**) and boiling MeOH containing fuming HCl. 1-*Keto*-3-*phenyl*-1 : 2 : 3 : 4-*tetrahydro*-2-*naphthylacetic acid* (**VII**), m.p. 171° [*oxime*, m.p. 151°, softens ~135°; non-cryst. Me ester (2 : 4-*dinitrophenylhydrazone*, m.p. 169—171°)], is obtained from (**III**) and H_2SO_4 in Et_2O at 0°, from the chloride of (**III**) with $AlCl_3$ [with an *isomeride*, m.p. 204—205°) (previous sintering)], from (**IV**) and $AlCl_3$ with an *isomeride*, m.p. 142—145°, from (**V**) and $AlCl_3$, and from the non-cryst. residue from (**III**) and H_2SO_4 in Et_2O at 0°. The best method is from the chloride (yield 65—70%). (**VII**) is characterised as a γ-CO acid by its transformation by N_2H_4,H_2O in boiling MeOH into 3-*keto*-5-*phenylhexahydro*-7 : 8-*benzocinnoline*, m.p. 191°. (**VII**) is dehydrated by conc. H_2SO_4 at room temp. into two *compounds*, $C_{18}H_{14}O_2$, m.p. 199—203° (*monodinitrophenylhydrazone*, m.p. 271°, darkens at 265°) and m.p. 131—135° (*monodinitrophenylhydrazone*, decomp. 230—231°) (cf. Knott, *Diss.*, *Frankfurt*, 1937). Provided the correct constitution has been assigned to (**VII**) the compounds must be partly hydrogenated derivatives of 1 : 2-benzanthracene or 2 : 3-benzphenanthrene. H. W.

2-Alkyl-3-phytyl-1 : 4-naphthaquinones.—See B., 1944, III, 100.

IV.—STEROLS AND STEROID SAPOGENINS.

Sex hormones and sterols. XVII. Side-chains of β- and γ-sitosterol. W. Dirscherl and H. Nahm (*Annalen*, 1943, **555**, 57—69).—Examination of the oxidation products of β- (**I**) and γ- (**II**) -sitosterol proves that the side-chain $\cdot CHMe{\cdot}[CH_2]_2{\cdot}CHEtPr^{\beta}$ is present in each. Optically it exerts a positive action in (**I**) and a negative effect in (**II**). In the two cases it differs in configuration at $C_{(24)}$, possibly also at $C_{(20)}$ and $C_{(17)}$. The yield of $COMe{\cdot}[CH_2]_2{\cdot}Bu^{\beta}$ obtained by the gradual addition of CrO_3 in 50% AcOH to cholesteryl acetate in boiling AcOH is materially improved by the addition of moderate amounts of $K_2S_2O_8$; "ceroyd" and SeO_2 appear ineffective and $K_2S_2O_8$ alone gives no ketone. Under similar conditions β-sitosteryl acetate affords $COMe_2$ and *ζ-methyl-*ε*-ethylheptan-β-one*, b.p. 80—92°/16 mm., $[\alpha]_D^{20}$ +2·54°±0·04°, 3·11±0·3° +3·11±0·3° in Et_2O (2 : 4-*dinitrophenylhydrazone*, m.p. 86—87°; *semicarbazone*, m.p. 141—142°, $[\alpha]_D^{23}$ +1·28°±0·6° in EtOH, $[\alpha]_D^{20}$ +4·5°±1° in $CHCl_3$), the structural identity of which with synthetic *dl*-$COMe{\cdot}[CH_2]_2{\cdot}CHEtPr^{\beta}$ is established rontgenographically. Similar treatment of the acetate of (**II**) leads to $COMe_2$ and (−)-ζ-methyl-ε-ethylheptan-β-one, $[\alpha]_D$ −2·4°±0·4° in Et_2O (*semicarbazone*, m.p. 140—142°). H. W.

Formation of cholestenone from cholesterol dibromide by removal of hydrogen bromide with collidine. F. Galinovsky (*Ber.*, 1941, **74**, [*B*], 1048—1049).—Boiling cholesterol dibromide in collidine and subsequent chromatography yields Δ^4-cholestenone. R. S. C.

Metabolism of steroids. IV. Ketonic acids derived from cholic acid. G. A. D. Haslewood (*Biochem. J.*, 1944, **38**, 108—111; cf. A., 1943, II, 199).—The series of six possible acids obtainable by oxidation to CO of one or two >CH·OH of cholic acid is completed by the prep. of 12-*hydroxy*-3 : 7-*diketocholanic acid* (**I**), m.p. 165—166° (with apparent change in η at 175°). Et 3 : 12-dihydroxy-7-ketocholanate (**II**), m.p. 155—157° (improved prep.), and AcCl–C_5H_5N–C_6H_6 at 0° give *Et* 12-*hydroxy*-7-*keto*-3-*acetoxycholanate* (**III**), m.p. 147—148°, oxidised by CrO_3–aq. AcOH to Et 7 : 12-*diketo*-3-*acetoxycholanate*, m.p. 145—147°. (**III**) and ArCOCl in C_5H_5N at 20°, then at 100°, afford *Et* 7-*keto*-12-p-*nitrobenzoyloxy*-, m.p. 159—160°, and *Et* 7-*keto*-12-3′ : 5′-*dinitrobenzoyloxy*-3-*acetoxycholanate*, m.p. 171—172°, converted by boiling 10N-HCl–EtOH, followed by CrO_3–aq. AcOH, into *Et* 3 : 7-*diketo*-12-p-*nitrobenzoyloxy*- (**IV**), m.p. 160—161°, and -3′ : 5′-*dinitrobenzoyloxy*-*cholanate*, m.p. 203—204°, respectively. The latter could not be hydrolysed without formation of highly coloured products, but (**IV**) and boiling KOH–MeOH give an acid, esterified (EtOH–H_2SO_4) to *Et* 12-*hydroxy*-3 : 7-*diketocholanate*, m.p. 168—169°, which with boiling aq. HCl–$COMe_2$ gives (**I**), with CrO_3–AcOH yields Et dehydrocholate, m.p. 218—220°, and with N_2H_4,H_2O–NaOEt–EtOH at 195—210°, followed by CrO_3, affords 12-ketocholanic acid. (**II**) and BzCl–C_5H_5N–C_6H_6 at 16—18° give *Et* 12-*hydroxy*-7-*keto*-3-*benzoyloxycholanate*, m.p. 138—139°, oxidised to *Et* 7 : 12-*diketo*-3-*benzoyloxycholanate*, m.p. 167—168°, and converted by boiling aq. K_2CO_3–EtOH into (probably) 12-*hydroxy*-7-*keto*-3-*benzoyloxycholanic acid*, m.p. 250—251° (decomp.). Me triacetylcholate and boiling 10N-HCl–MeOH, followed by CrO_3–aq. AcOH, give *Me* 3-*keto*-7 : 12-*diacetoxycholanate*, m.p. 190—191°, convertible by N_2H_4,H_2O–NaOEt–EtOH at 200—210° into 7 : 12-dihydroxycholanic acid, m.p. 205°. A. T. P.

Sapogenin derivatives.—See B., 1944, III, 101.

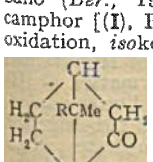
V.—TERPENES AND TRITERPENOID SAPOGENINS.

Synthesis of safranic acid. G. Wendt (*Ber.*, 1941, **74**, [*B*], 1242—1251).—Safranal resists oxidation to the acid by air or $AgNO_3$–NaOH, and its oxime in warm Ac_2O gives a nitrile, b.p. 86°, which resists hydrolysis. *β-cyclo*Geranic acid (**I**) (prep. from *β-cyclo*citral by shaking in air), m.p. 93—94° (p-$C_6H_4Br{\cdot}CO{\cdot}CH_3$ ester, m.p. 103—104°), is much more slowly hydrogenated (PtO_2; AcOH) than is its α-isomeride; similarly, the latter, but not (**I**), readily adds Br. With Br–CCl_4 in light or with C_5H_5N,H_2SO_4–Br, (**I**) gives the 3-*Br-acid* [3-*bromo*-2 : 6 : 6-*trimethyl*-Δ^2-*tetrahydrobenzoic acid*] (**II**) (65—70%), m.p. 97—98°, converted by boiling H_2O or NaOH–H_2O–MeOH into the 3-*OH-acid* (**III**) (80—90%), m.p. 184° [*Me* ester, b.p. ~100° (bath)/0·01 mm.] (Kuhn–Roth determination yields 1·2 AcOH) (cf. Tiemann, A., 1901, i, 158). With CrO_3 (≡3 O) in H_2SO_4–AcOH–H_2O at 20°, (**I**) gives $CO_2H{\cdot}CMe_2{\cdot}[CH_2]_2{\cdot}CO_2H$, AcOH, and CO_2, but with CrO_3 (≡1 O) gives 3-keto-2 : 6 : 6-trimethyl-Δ^1-tetrahydrobenzoic acid, m.p. 192° [*semicarbazone* m.p. 240° (decomp.)] (cf. *loc. cit.*), which proves the structure of (**II**) and

(III). With H_2SO_4–HCO_2H, (III) gives a *CHO* derivative, m.p. 179° (decomp.). In C_5H_5N or collidine at 160°, (II) gives *safranic* [2 : 2 : 6-*trimethyl*-2 : 3-*dihydrobenzoic*] *acid* (IV), m.p. 63—64°, b.p. 85—90°/0·001 mm. (p-C_6H_4Br·*CO*·CH_3 ester, m.p. 102°). The structure of (IV) is proved by the resemblance of its absorption spectrum (max. at 291 mμ. in EtOH) to that of 2 : 3-dihydro-*o*-toluic acid (max. at 283 mμ.); the corresponding aldehydes show similarly max. at 323 and 317 mμ., respectively. In presence of Pt–SiO_2 in AcOH, (IV) absorbs 1 H_2 fast and a second mol. more slowly; partial hydrogenation yields (I). With HBr–$CHCl_3$, (III) gives 4-bromo-2 : 6 : 6-trimethyl-Δ^1-tetrahydrobenzoic acid, which is decarboxylated by warm H_2O. NaOH–KOH and a little H_2O at 210° convert (II) into a *dehydrocyclogeranic acid*, $C_{10}H_{14}O_2$, m.p. 130°, of unknown structure. (III) and (IV) have no termone action on cells of *Chlamydomonas eugametos* f. *synoica*. R. S. C.

Temisin. II. Y. Asahina and T. Ukita (*Ber.*, 1941, **74**, [*B*], 952—963; cf. A., 1940, II, 330).—Temisin (I) is shown to be the *2-lactone* of α-2 : 6-dihydroxy-4-methyl-4-vinyl-3-*iso*propenyl*cyclo*hexylpropionic acid. Formation of 1 : 7-$C_{10}H_6$MeEt by Se at 270—280° (Nakamura *et al.*, A., 1933, 651; 1934, 1007) is confirmed by mixed m.p. determinations with the product from santonin. Na–*iso*-C_5H_{11}·OH reduces the lactone group of (I), yielding *temisol* [β-2 : 6-*dihydroxy*-4-*methyl*-4-*vinyl*-3-iso*propenyl*cyclo*hexyl*-n-*propyl alcohol*] (II), m.p. 126°, $[\alpha]_D^{16}$ +14·93° in EtOH, which with H_2–PtO_2 in AcOH gives *β-tetrahydrotemisol* [the 4-*ethyl*-3-iso*propyl* compound], m.p. 128—130°, $[\alpha]_D$ +24·61° in EtOH; this is isomeric at $C_{(3)}$ with α-tetrahydrotemisol, which may indicate presence of 4-CMe_2·: in place of 4-CH_2·CMe_2 in (II) or its formation by the alkali during the reduction (cf. below); the fact that two C:C survive Na–C_5H_{11}·OH proves that they are not conjugated. Temisone [the *lactone* of α-2-hydroxy-6-keto-4-methyl-4-vinyl-3-*iso*propenyl*cyclo*hexylpropionic acid] (III) with O_3 in $CHCl_3$ yields CH_2O (0·37 mol.) but no $COMe_2$, proving absence of CMe_2:. Hydrolysis of tetrahydrotemisone by warm 0·1N-NaOH gives the oily OH-acid, which is dehydrated by boiling Ac_2O–NaOAc to the *lactone* (IV), m.p. 145°, of the enol form of α-2-*keto*-4-*methyl*-4-*ethyl*-5-iso*propyl*cyclo*hexylidenepropionic acid* (V), m.p. 129—130°. (IV) is unaffected by $KMnO_4$ or Ac_2O–NaOAc, gives a colour with $C(NO_2)_4$ but not with Na nitroprusside, absorbs Br slowly in AcOH, absorbs 3 H_2 (PtO_2; AcOH; to give an oily deoxy-acid), and with hot NaOH–EtOH–H_2O gives (V) and mixed isomeric *cyclo*hexenylpropionic acids, sinter ~75°, m.p. 90°. (V) decolorises $KMnO_4$, does not react with $C(NO_2)_4$, NH_2·CO·NH·NH_2, *p*-NO_2·C_6H_4·NH·NH_2, H_2–PtO_2–AcOH, or NaOI, with boiling Ac_2O–NaOAc regenerates (IV), and with O_3 in cold $CHCl_3$ gives AcCO·H and *β-methyl-β-ethyl-β'-iso*propyladipic *acid*, m.p. 134°, $[\alpha]_D^{26}$ +5·94° in EtOH, which proves the cyclic nature of one (*cyclo*hexane) ring. Similarly, (III) with 1 equiv. of 0·1N-NaOH at 100° gives a colourless, oily OH-acid, converted by boiling Ac_2O–NaOAc into the *lactone* (VI), m.p. 79°, $[\alpha]_D$ −74·83° in C_6H_6, of the enol form of α-2-*keto*-4-*methyl*-4-*vinyl*-5-iso*propenyl*cyclo*hexylidenepropionic acid* (VII), m.p. 162·5°; (VI) is also obtained directly from (III) by Ac_2O–NaOAc. H_2–PtO_2 reduces (VI) in AcOH to an oily acid, boiling NaOH–EtOH–H_2O converts it into (VII) and mixed isomeric cyclo*hexenylpropionic acids*, sinters ~110°, m.p. 125°. Hydrogenation (PtO_2) of (VII) in AcOH gives (V). An excess of NaOH in hot EtOH–H_2O converts (III), with isomerisation, into α-6-*keto*-4-*vinyl*-3-iso*propylidene*-Δ^1-cyclo*hexenylpropionic acid* (VIII), m.p. 108·5°, $[\alpha]_D^{16}$ +162·99° in EtOH [*p-nitrophenylhydrazone*, m.p. 126°; absorbs 3 H_2 (PtO_2; AcOH)], which with O_3 in $CHCl_3$ at 0° gives $COMe_2$, EtCO·H, CO_2H·$CHMe$·CH_2·CO_2H, CH_2O (0·148 mol.), and presumably, 3 CO_2; these products and the isoprene rule confine the structure of (VIII) to three possibilities, of which one is excluded because formation of the C:C from a β-OH-acid excludes a C:C·C·CO grouping and a second is excluded because the absorption max. of (VIII) at 3180 A. (log ε 4·27) indicates a C:C·C:C·CO. These facts prove the structure of (I) etc. Since hydrolysis and subsequent esterification of (I) causes no re-lactonisation, the free OH and the CHMe·CO are in *trans*-relation. In hot NaOI–NaOH, (III) gives CHI_3 by prior transformation into (VIII) and hydrolysis thereof to $COMe_2$.
R. S. C.

Formation of *d*-santenone from π-aldehydocamphor. Configuration of santenone and santenic acid. M. Ishidate and T. Sano (*Ber.*, 1941, **74**, [*B*], 1189—1194).—When *trans*-π-ketocamphor [(I), R = CHO] is kept in air, it rapidly yields, by autoxidation, *iso*ketopinic acid (II) [(I), R = CO_2H] and, by fission, HCO_2H and d-α-*santenone* (III) [(I), R = H], m.p. 56—59°, $[\alpha]_D^{22}$ +11·4° in EtOH [*semicarbazone*, m.p. 235—236° (decomp.)]. Fission also occurs when [(I), R = CHO] is kept in H_2O–N_2, the change being catalysed by O_2 or OH′ and prevented by H_2SO_4. (III) is an optically pure component of Aschan's *dl*-α-santenone (A., 1933, 1166). (II) is stable in boiling C_5H_5N + Cu-bronze and in boiling 10% KOH and is thus not an intermediate in the fission. With $KMnO_4$ in 1% KOH, (III) gives d-cis-α-*santenic acid* (IV), $[CH_2]_2<\begin{matrix}CH(CO_2H)-\\CMe(CO_2H)\end{matrix}>CHMe$ (CO_2H and Me on $C_{(7)}$ all *cis*), m.p. 151—152°, $[\alpha]_D^{20}$ +38·31° in EtOH, which with AcCl at room temp. gives the *anhydride*, m.p. 129—130°, reconverted into (IV) by hydrolysis. (IV) is better obtained by converting (III) by SeO_2 in boiling AcOH into its derived 1 : 2-diketone, *α-santenequinone*, m.p. 73—74°, b.p. 110—112°/12 mm., $[\alpha]_D$ −75·38° in EtOH, and oxidising this with H_2O_2–EtOH–Na_2CO_3. (IV) cannot be isomerised to the *trans*-acid by, *e.g.*, conc. HCl–AcOH at 190°. R. S. C.



Examination of the sesquiterpene alcohol schairol, from *Ferula pyramidata* (Kar. *et* Kir.), Eug. Kov. (*syn. F. paniculata*, LDB). N. P. Kirialov (*J. Gen. Chem. Russ.*, 1943, **13**, 145—154).—Schairol (I), heated with 90% HCO_2H, yields a *hydrocarbon*, $C_{15}H_{24}$, an oil; with Se (7 hr. at 250—280°) it affords an azulene *hydrocarbon*, $C_{15}H_{18}$, b.p. 131—132°/2 mm. (*picrate*, m.p. 111—113°). (I) is oxidised ($KMnO_4$ in aq. $COMe_2$) to a *substance* (II), $C_{15}H_{24}O(OH)_2$, m.p. 221—222°, and a *substance*, $C_{15}H_{25}(OH)_3$, m.p. 102—103°, $[\alpha]_D$ +2·83° in aq. EtOH. (II), heated in a sealed tube with KOH–EtOH (8 hr. at 100°), affords a *substance*, $C_{15}H_{22}O$, b.p. 128—130°/5 mm., $[\alpha]_D$ +14·0° in aq. EtOH, from which a hydrocarbon, possibly cadalene, is obtained by treatment with Se. Hydrogenation of (I) in AcOH solution, using $PdCl_2$ or PtO_2 catalysts, was unsuccessful. The results support the view that (I) is an isomeride of guaiol.
R. T.

Sapogenin.—See B., 1944, III, 101.

VI.—HETEROCYCLIC.

Polymerisation processes. IX. Dimeric methyl vinyl ketone. K. Alder, H. Offermanns, and E. Rüden. **X. Dimeric acraldehyde.** K. Alder and E. Rüden. **XI. General scheme of dimerisation of αβ-unsaturated aldehydes and ketones.** K. Alder, H. Offermanns, and E. Rüden (*Ber.*, 1941, **74**, [*B*], 905—920, 920—926, 926—929).—IX. The dimeride of CH_2:CH·COMe is shown to be 6-*acetyl*-2-*methyl*-Δ-*dihydropyran* (I). Its ethylenic linking is susceptible to numerous addition reactions. Heating CH_2:CH·COMe with 1% of quinol (to depress formation of higher polymers) at 145° (autoclave) for 22 hr. gives ~55% of (I) with a trimer and other polymers. (:CH·CO)$_2$O and (I) do not react at 200°. 1 H_2 is absorbed by (I) in MeOH in presence of Pd–$CaCO_3$, yielding 2-*acetyl*-6-*methyltetrahydropyran* (II), b.p. 64°/12 mm. (*semicarbazone*, m.p. 175°; p-*OMe*·C_6H_4·*CH*: derivative, m.p. 174—175°). MgPhBr (only 1 mol. consumed) and (II) in Et_2O, later at the b.p., give a carbinol, b.p. 150—170°/11 mm., dehydrated by $KHSO_4$ at 180—190° to 2-*α-phenylvinyl-* [? 2-*α-phenylethylidene-*]6-*methyltetrahydropyran*, b.p. 138—140°/12 mm. With aq. $KMnO_4$–CO_2 at room temp. and then CH_2N_2–Et_2O, (II) gives δ-*n*-hexolactone (proof of ring structure), identified by (i) conversion by NH_3–EtOH at 100° into δ-*hydroxy*-n-*hexoamide*, m.p. 74°, which is also obtained from the synthetic δ-lactone and depresses the m.p. (74°) of the isomeric γ-OH-amide, and (ii) oxidation by HNO_3 to glutaric (III) and succinic (IV) acids. $KMnO_4$–CO_2 and (I) yield (III), which proves the location of the C:C. HNO_3–H_2O [83 (*d* 1·4) : 23 c.c.] and (I) yield, after methylation, $Me_2C_2O_4$, $(CH_2$·$CO_2Me)_2$, OH·$CHMe$·CO_2Me (V), the *Me* ester, m.p. 45—46°, of the lactone of α-hydroxyglutaric acid [converted by 57% HI into (III); dihydrazide, m.p. 157—158°), and Me_2 fumarate [derived from (V)]. With NaOBr at 30°, (I) gives exothermally $CHBr_3$ and 2-methyltetrahydropyran-6-carboxylic acid (*Me* ester, b.p. 205—210°; *hydrazide*, m.p. 92—93°) (proof of COMe). 2% HCO_2H at room temp. converts (I) into *n*-octan-γ-ol-βη-dione, b.p. 147°/13 mm. [*disemicarbazone* (VI), m.p. 217°; *bis*-2 : 4-*dinitrophenylhydrazone*, m.p. 186°, also obtained by heating (I) with 2 : 4-$(NO_2)_2C_6H_3$·NH·NH_2 in EtOH], probably by way of 2-hydroxy-6-acetyl-2-methyltetrahydrofuran. With aq. NH_2·CO·NH·NH_2,HCl–NaOAc, first warm and then at 0°, (I) gives its *semicarbazone*, m.p. 176°, and, by addition prior to fission, (VI). EtOH or MeOH in AcOH adds exothermally to (I), yielding 2-ethoxy- [*semicarbazone*, m.p. 180°; regenerates (I) and EtOH when distilled at 12 mm.] and 2-methoxy-6-acetyl-2-methyltetrahydropyran (*semicarbazone*, m.p. 183°), respectively. H_2O_2 and (I) in AcOH give exothermally *di*-2-*methyl*-6-*acetyltetrahydro*-2-*pyranyl peroxide*, m.p. 124—125°. With N_2H_4,H_2O and then KOH, (II) gives 2-*methyl*-6-*ethyltetrahydropyran*, b.p. 34—35°/15 mm., and an isomeric, unsaturated alcohol, b.p. 81—82°/13 mm.

X. The dimeride of CH_2:CH·CHO is proved to be 6-*formyl*-Δ^2-*dihydropyran* (VII). It is obtained in 40—45% yield by heating at 170° with 1% of quinol, has b.p. 145—148°, gives a semicarbazone, m.p. 123—124°, and with aq. $KMnO_4$–CO_2 gives (IV) (~100%). H_2–PtO_2 reduces (VII) in MeOH to 2-*formyltetrahydropyran* (VIII), b.p. 156—159° (semicarbazone, m.p. 154°), which with $KMnO_4$–CO_2 and then HNO_3 gives (III) and (IV), and with MgPhBr–Et_2O gives a carbinol, b.p. 150—160°/11 mm., whence $KMnO_4$–CO_2 yields quantitatively (III), (IV), and BzOH. With N_2H_4,H_2O in MeOH at ~50° and then KOH, (VIII) gives 2-*methyltetrahydropyran*, b.p. 104—106° (and a substance, b.p. 160—165°), which is also obtained by dehydrating (by distillation) and then reducing (H_2–PtO_2; MeOH) OH·$[CH_2]_4$·COMe.

XI. The unidirectional 1 : 4 addition of C:C to C:C·C:O during dimerisation of CH_2:CH·COX (X = H or Me) is a general phenomenon. It is reported (without details) also for X = Ph, but in this case the cryst. dimeride can undergo further self-condensation.

Other cases are X = Et and dimerisation of quinonemethides to coumarin derivatives. R. S. C.

New heterocyclic compound with antihæmorrhagic (vitamin-*K*) activity. P. Meunier and C. Mentzer (*Compt. rend.*, 1942, **215**, 259—261).—*o*-OH·C_6H_4·CO_2Me is slowly converted by boiling $(EtCO)_2O$ into *Me* o-*propoxybenzoate*, b.p. 154°/14 mm., transformed by Na at 165—180° into 2 : 4-*dihydroxy*-3-*methylchroman* (**I**), m.p. 229—230° (decomp.), which could not be obtained by the action of $NaNH_2$ and MeI on benzotetronic acid. The physiological activity of (**I**) is ~0·1 of that of 2-methylnaphthaquinone and is in harmony with the hypothesis that the group ·CO·CH:CH_2 ⇌ :C:C(OH)·CH_2· is responsible for antihæmorrhagic activity. H. W.

Chromans.—See B., 1944, II, 101.

Natural chromones. II. Constitution of visnagin (from *Ammi visnaga*). E. Spath and W. Gruber (*Ber.*, 1941, **74**, [*B*], 1492—1500).—Mother-liquors from kellin (A., 1938, II, 111) yield 0·045% of *visnagin*, m.p. 144—145° (oxonium nitrate), which is shown to be 5-*methoxy*-2-*methylfurano*-3′ : 2′-6 : 7-*chromone*. With H_2O_2 in 5% NaOH at 20° it gives $H_2C_2O_4$ and furan-2 : 3-dicarboxylic acid (23%), and in boiling 1% NaOH is hydrolysed to AcOH and *visnagone* [5-*hydroxy*-4-*acetyl*-3-*methoxybenzfuran*] (**I**), m.p. 109—111° (brownish-green colour with $FeCl_3$), sol. in alkali, whence Ac_2O and NaOAc at 150—155° give 3-*acetylvisnagin*, m.p. 192—193°. In 1 : 1 NaOH–KOH at 205° (**I**) gives *s*-$C_6H_3(OAc)_3$. Et_2SO_4–20% aq. KOH converts (**I**) into its *Et ether*, m.p. 153—154°, reduced by Hg–Zn–aq. HCl to 3-*methoxy*-5-*ethoxy*-4-*ethylbenzfuran* (74%), m.p. 54—57°, which with O_3 in $CHCl_3$ at −5° gives 6 : 3 : 2 : 4 : 1-OH·C_6HEt(OMe)(OEt)·CHO (**II**) (58%), an oil [*p*-*nitrophenylhydrazone*, m.p. 218—220° (decomp.)]. With Et_2SO_4–10% KOH, (**II**) gives 6 : 4 : 3 : 2 : 1-$(OEt)_2C_6$HEt(OMe)·CHO (**III**), b.p. 124—126°/0·01 mm. (*semicarbazone*, m.p. 182—183°), whence $KMnO_4$–$COMe_2$–$MgSO_4$ at 50° yields 2-*methoxy*-4 : 6-*diethoxy*-3-*ethylbenzoic acid* (**IV**), m.p. 118—120° (decomp.; vac.). 2 : 4 : 6 : 1-$(OH)_3C_6H_2$·COMe and Zn–Hg–HCl–H_2O–EtOH give 2 : 4 : 6 : 1-$C_6H_2Et(OH)_3$ (76%), m.p. 123—125°, converted by HCN–HCl–Et_2O into 2 : 4 : 6-*trihydroxy*-3-*ethylbenzaldehyde* (78%), m.p. 174—176°. With EtI and K_2CO_3 in boiling $COMe_2$ this gives the 4 : 6-*Et*$_2$ *ether* (76%), m.p. 94—95° [*p*-nitrophenylhydrazone, m.p. 254—256° (decomp.; vac.)], whence Me_2SO_4–20% KOH at 70° yields (**III**) (*p*-*nitrophenylhydrazone*, *forms*, m.p. 180—182° and 169—171°), and thence (**IV**). R. S. C.

Synthesis of chroman derivatives having the ring-system of α-tocopherol. Synthesis of *iso*-α-tocopherol from (IV) ψ-cumene, (V) ψ-cumoquinol monomethyl ether. W. John and (IV) P. Günther, (V) F. H. Rathmann (*Ber.*, 1941, **74**, [*B*], 879—890, 890—898).—The synthesis of α-tocopherol analogues described in Part IV below uses accessible starting materials but requires ≮3 mols. of Grignard reagent in the last stage; that described in Part V needs only 2 mols. of Grignard reagent, but the starting materials are less accessible.

IV. 2 : 4 : 5 : 1-$C_6H_2Me_3$·CHO [prep. by Gattermann synthesis from ψ-cumene (**I**) in 70% yield] (32 g.), b.p. 105—110°/0·5 mm., with $COMe_2$ and NaOEt in EtOH at, successively, 0°, room temp., and 35° gives α-2 : 4 : 5-*trimethylphenyl*-Δ$^{\alpha}$-*buten*-γ-*one* (**II**) (24 g.), m.p. 51° [*semicarbazone*, m.p. 220° (decomp.)], and a small amount of αε-*di*-2 : 4 : 6-*trimethylphenyl*-Δ$^{\alpha\delta}$-*pentadien*-γ-*one*, m.p. 165·5°; use of aq. NaOH leads to a difficultly separable 3 : 1 mixture of (**II**) and α-2 : 4 : 5-*trimethylphenyl*-n-*butan*-α-*ol*-γ-*one*, m.p. 92°. Hydrogenation (Pd-black; EtOH) of (**II**) gives mainly β-2 : 4 : 5-*trimethylphenylethyl Me ketone* (**III**), m.p. 55° (semicarbazone, m.p. 185—187°) (and ? isomerides), which with MgMeI gives δ-2 : 4 : 5-*trimethylphenyl*-β-*methyl*-n-*butan*-β-*ol*, m.p. 44° (*dinitrobenzoate*, m.p. 134°; could not be satisfactorily nitrated). Adding crude (**III**) in light petroleum to KNO_3–H_2SO_4 at −5° and then stirring at room temp. for a few min. gives β-3 : 6-*dinitro*-2 : 4 : 5-*trimethylphenylethyl Me ketone* (**IV**), m.p. 136·5°, and a very small amount of a *substance*, $C_{13}H_{16}O_6N_2$, m.p. 151°. With $SnCl_2$–conc. HCl–AcOH at ~80°, (**IV**) gives the diamine stannichloride, which by repeated treatment with CrO_3 in 2N-H_2SO_4 at, successively, 5°, room temp., and 30° yields ~40—45% of 1 : 2 : 3 : 5 : 6 : 4-O:C_6Me_3([CH_2]$_2$·COMe):O, m.p. 56°, whence the quinol (**V**), m.p. 125° (lit., 122°), is best obtained by Zn dust–H_2SO_4–MeOH–H_2O at room temp. CH_2O–HCl converts (**I**) at 70° into 2 : 4 : 5-*trimethylbenzyl chloride* (**VI**) (40—45%), b.p. 98—108°/1 mm., and a small amount of *di*(*chloromethyl*)-ψ-*cumene*, m.p. 99—101°. With CHAcNa·CO_2Et in C_6H_6 at room temp. and then the b.p., (**VI**) gives an oily ester, which by hydrolysis (10% KOH–MeOH at room temp.) and distillation affords crude (**III**), best purified at the $(NO_2)_4$-stage (**IV**). *n*-$C_{14}H_{29}$·MgCl (prep. from Mg activated by $C_{14}H_{29}$Br, I, and MeI) (3 mols.) and (**V**) in Et_2O–C_6H_6–N_2 yield a carbinol, cyclised by boiling 10% *p*-C_6H_4Me·SO_3H–AcOH and by Zn dust and then HBr in AcOH to "iso-α-*tocopherol*" [6-*hydroxy*-2 : 5 : 7 : 8-*tetramethyl*-2-n-*tetradecylchroman*] (**VII**), m.p. 64°, which is purified by way of its *allophanate*, m.p. 174—175° [absorption max. at 280 mμ. (ε 1740)]; this is separated from $C_{30}H_{56}$ by chromatography and from *cetylurethane*, m.p. 93°, and *cetyl allophanate*, m.p. 153°, by crystallisation. (**VII**) reduces $AgNO_3$–EtOH and in conc. HNO_3–EtOH gives a red colour. $C_{14}H_{29}$·MgBr yields more hydrocarbon.

V. 1 : 2 : 3 : 6 : 4-OH·C_6HMe$_3$·OMe (**VIII**), $Zn(CN)_2$, $AlCl_3$, and HCl in C_6H_6 at 0° and then 40° give only small amounts of 3-*hydroxy*-6-*methoxy*-2 : 4 : 5-*trimethylbenzaldehyde*, m.p. 107—108°, and thence α-3-*hydroxy*-6-*methoxy*-2 : 4 : 5-*trimethylphenyl*-Δ$^{\alpha}$-*buten*-γ-*one*, m.p. 104°, and β-3-*hydroxy*-6-*methoxy*-2 : 4 : 5-*trimethylphenylethyl Me ketone* (**IX**), m.p. 76°. 40% CH_2O and conc. HCl at room temp. convert (**VIII**) into 3-*hydroxy*-6-*methoxy*-2 : 4 : 5-*trimethylbenzyl chloride* (~75%) (**X**), m.p. 128°; the corresponding 6-*OEt*-, m.p. 123—124°, 6-*OPr*-, m.p. 117—118°, and 6-*OBu*-compound, m.p. 83—85°, are similarly prepared. With CHAcNa·CO_2Et in C_6H_6, (**X**) gives *Et* 3-*hydroxy*-6-*methoxy*-2 : 4 : 5-*trimethylbenzylacetoacetate* (not quite pure), m.p. 52—53°, and thence (0·5N-NaOH) the derived *acid*, m.p. 128° (decomp.), which at slightly >100° yields almost 50% (calc. on ψ-cumoquinol) of (**IX**), m.p. 81°. With MgMeI (2 mols.) in Et_2O–C_6H_6, (**X**) gives δ-3-*hydroxy*-6-*methoxy*-2 : 4 : 5-*trimethylphenyl*-β-*methyl*-n-*butan*-β-*ol*, m.p. 104—105°, converted by AgOAc into 1 : 2 : 3 : 5 : 6 : 4-O:C_6Me_3([CH_2]$_2$·CMe_2·OH):O, m.p. 55°, whence *p*-C_6H_4Me·SO_3Me–AcOH or Zn dust–HBr–AcOH yields 6-hydroxy-2 : 2 : 5 : 7 : 8-pentamethylchroman. With MgRBr in Et_2O–C_6H_6, (**IX**) similarly gives α-3-*hydroxy*-6-*methoxy*-2 : 4 : 5-*trimethylphenyl*-γ-*methyl*-n-*pentan*-γ-*ol*, m.p. 98·5—99·5°, -n-*heptan*-γ-*ol*, m.p. 88°, and -n-*pentadecan*-γ-*ol*, m.p. 69—71°. *n*-$C_{11}H_{23}$·MgCl yields an oily carbinol, converted by AgOAc and then HBr–AcOH into (**VII**), which is purified as above, giving an allophanate, m.p. 176° [absorption max. at 280 mμ. (ε 1740) and min. at 250 mμ. (ε 200)]. R. S. C.

Furo-coumarone group. II. 3 : 3′-Dimethyl-6′ : 7′-furo-coumarone. D. B. Limaye and V. V. Nagarkar (*Rasāyanam*, 1943, **1**, 255—257; cf. A., 1941, II, 374).—2 : 4 : 1 : 3-$C_6H_2Ac_2(OH)_2$ (Na H salt) with CH_2Br·CO_2Et gives *Me* 2 : 4-*diacetylresorcinol*-1-*carboxylate* (**I**), m.p. 168° (*Et*, m.p. 75°, and *Me* ester, m.p. 69°). (**I**) with NaOAc and Ac_2O gives 4-*acetoxy*-5-*acetyl*-3-*methylcoumarone*, m.p. 108°, which yields 4-*hydroxy*-5-*acetyl*-3-*methylcoumarone* (**II**), m.p. 70° (*semicarbazone*, m.p. 255°; *benzoate*, m.p. 118°; *Me ether*, m.p. 72)°. (**II**) (Na salt) with CH_2Br·CO_2Et gives, after hydrolysis, *Me* 5-*acetyl*-3-*methylcoumarone*-4-*carboxylate*, which with NaOAc and Ac_2O yields 3 : 3′-dimethyl-6′ : 7′-furo-coumarone, m.p. 27°. D. G.

Coumarin-γ-pyrone group. IV. 4 : 2′-Dimethyl-3′-acetyl-7 : 8-coumarin-γ-pyrone and 4 : 4′-dimethyl-7 : 8-coumarin-α-pyrone. D. B. Limaye and K. M. Kulkarni (*Rasāyanam*, 1943, **1**, 251—254).—8-Acetyl-4-methylumbelliferone (*acetate*, m.p. 191°) with Ac_2O and NaOAc gives 4 : 4′-*dimethyl*-1′ : 2′-*pyrono*-5′ : 6′-8 : 7-*coumarin*, m.p. 242°, and (main product) 5′-*acetyl*-4 : 6′-*dimethyl*-1′ : 4′-*pyrono*-5′ : 6′ : 8 : 7-*coumarin* (**I**), m.p. 265°. (**I**) with aq. NaOH gives 4-*methylumbelliferone*-8-*carboxylic acid* (**II**), m.p. 263° (decomp.). (**II**) is also obtained from γ-resorcylic acid (A., 1936, 854) with CH_2Ac·CO_2Et and H_2SO_4. (**II**) gives a 7-*OMe*-derivative (**III**), m.p. 246° (decomp.) [Me (**IV**), m.p. 189°, and Et ester, m.p. 163°]. (**III**) and (**IV**) on hydrolysis (NaOH aq.) yield 2-*hydroxy*-4-*methoxy*-3-*carboxy*-β-*methylcinnamic acid*, m.p. 194°, and (**IV**) with KOH in EtOH gives 2 : 4-*dimethoxy*-3-*carboxy*-β-*methylcinnamic acid*, m.p. 208° (decomp.). D. G.

Constitution of paraldol.—See A., 1944, II, 183.

Plant growth substances. XXXIV. β-Biotin.—See A., 1944, III, 487.

***iso*Thioindigotin.** P. Chovin (*Compt. rend.*, 1942, **215**, 419—420).—1-Hydroxythionaphthen (**I**) is converted by PhNO or *p*-NO·C_6H_4·NMe_2 into *leuco*iso*thioindigotin*, m.p. 260° (decomp.), which gives only a violet, non-cryst. resin when its oxidation to iso*thioindigotin* (**II**) is attempted. A similar resin is produced when (**I**) is treated with S_2Cl_2, $SOCl_2$, or $FeCl_3$. In EtOH at 0° (**I**) is transformed by SeO_2 into (**II**), m.p. 224° (decomp.), which is darker in colour than thioindigotin. H. W.

2 : 4-Diarylpyrroles. IV. Formation of acylated 5-amino-2 : 4-diphenylpyrroles from β-benzoyl-α-phenylpropionitrile and some notes on the Leuckart reaction. W. H. Davies and M. A. T. Rogers (*J.C.S.*, 1944, 126—131).—CH_2Bz·CHPh·CN (**I**) with HCO_2NH_4 gives 2 : 2′ : 4 : 4′-tetraphenylazadipyrromethine (**II**), but with HCO·NH_2 affords mainly a colourless compound, m.p. 172°, now shown to be a *formyl* derivative of 5-amino-2 : 4-diphenylpyrrole (**III**) (cf. Rogers, A., 1944, II, 80), which has been synthesised from the parent pyrrole and the mixed anhydride of HCO_2H and AcOH. The mechanism of this reaction and the formation of (**II**) from (**I**) and HCO_2NH_4 or HCO·NH_2 are discussed and inter-related. The mechanisms of the Leuckart reaction and of its Ott–Ingersoll modification are shown to involve different intermediates which may, in the case of certain ketones, result in different products. The following derivatives of (**III**) have been isolated in readily interconvertible isomeric forms: *formyl*, m.p. 172° and 176°, *Ac*, m.p. 171°, 176°, and 192°, *acetyl-formyl*, m.p. 134°, 139°, and 152°, Ac_2, m.p. 186—188°, and Ac_3, m.p. 111—112°. F. R. S.

Electronic resonance of 1-methyl-2-piperidone.—See A., 1944, I, 143.

Nicotinyl chloride. M. Lora Tamayo and A. Vargas (*Anal. Fis. Quim.*, 1942, **38**, 179—183).—Nicotinyl chloride hydrochloride (cf. Spath and Spitzer, A., 1926, 958) is converted by boiling C_5H_5N, or by prolonged exposure over $CaCl_2$ in vac., into the high-melting form of nicotinyl chloride (cf. Meyer, A., 1901, i, 407). The low-melting form of Meyer and Graf (A., 1928, 1379) was not isolated. F. R. G.

Synthesis of hydroxy-derivatives of 2-methylpyridine-3 : 5-dicarboxylic acid esters. E. Ochiai and Y. Ito (*Ber.*, 1941, **74**, [*B*], 1111—1114).—OEt·CH:C(CO_2Et)$_2$ (**I**) and NH_2·CMe:CH·CO_2Et at 100° (40 hr.) give *Et*$_2$ *hydroxy-2-methylpyridine-3 : 5-dicarboxylate*, m.p. 205°, converted by hot 5% KOH–MeOH into an *Et H* ester, m.p. 225°, and then into the *dicarboxylic acid*, m.p. 305°. Decarboxylation of the acid by Cu chromite in quinoline at 300—315° (bath) gives 6-hydroxy-2-methylpyridine, m.p. 158° (picrate, m.p. 149·5—150°), whence the orientation of the products follows. (**I**), $CH_2Ac·CO_2Et$, and HCl gas at room temp. give, with partial decarboxylation, *Et 4-hydroxy-2-methylpyridine-3-carboxylate*, m.p. 207°, converted by $POCl_3$ at 150° into *Et 4-chloro-2-methylpyridine-3-carboxylate*, m.p. 64°, which with Zn dust in dil. HCl at 100° gives Et 2-methylpyridine-3-carboxylate (*picrate*, m.p. 146—147°; hydrochloride, decomp. 225°). CHAcNa·CO_2Et, (**I**), and Na in hot C_6H_6 give *Et*$_2$ *4-hydroxy-2-methylpyridine-3 : 5-dicarboxylate*, m.p. 156—157°, which with NH_3–EtOH (saturated at <0°) at 100° gives the derived *diamide*, decomp. 321°, and *Et 4-hydroxy-(?)5-carboxylamido-2-methylpyridine-(?)3-carboxylate*, m.p. 252°. R. S. C.

Salts of pyridine-2 : 6-dicarboxylic acid.—See B., 1944, III, 101.

Two new syntheses of quinoline from benzene and glycerol. L. Bert (*Compt. rend.*, 1942, **215**, 415—417).—C_6H_6 is condensed with CH$_2$Cl·CH:CHCl [obtained by dehydration of OH·CH(CH_2Cl)$_2$] directly (Friedel–Crafts) or indirectly through MgPhBr to $CH_2Ph·CH:CHCl$, which when added gradually to a deficiency of H_2SO_4–HNO_3 at −10° gives a mixture (**I**) of *o*- and *p*-$NO_2·C_6H_4·CH:CH·CHCl$. This when heated with an alcohol ROH (usually R = Me, Et, or Bu$^\alpha$) and excess of KOH affords a mixture (**II**) of *o*- and *p*-$NO_2·C_6H_4·CH:CH·CH_2·OR$ converted into *o*- (**III**) and *p*-$NO_2·C_6H_4·CHO$, separable from one another by distillation with steam or through their compounds with $NaHSO_3$. Alternatively (**I**) is nitrated by fuming HNO_3–Ac_2O mainly to (**III**), which is reduced ($FeSO_4$–NH_3) to *o*-$NH_2C_6H_4·CHO$ and thence transformed into quinoline (**IV**) according to Friedlander. (**I**) is readily reduced (Fe + HCl) to the corresponding amines, which are easy to separate from one another. The *o*-compound is converted by excess of KOH and boiling ROH (R is any radical) into *o*-$NH_2·C_6H_4·CH:CH·CH_2·OR$, transformed by HCl under pressure into *o*-$CH_2Cl·CH:CH·C_6H_4·NH_2$,HCl. This with aq.-alcoholic $(CH_2)_6N_4$ passes into $CHO·CH:CH·C_6H_4·NH_2$,HCl, readily converted into (**IV**). Experimental details are not given. H. W.

Reaction product from hydrazine and 4-chloroquinaldine. E. Koenigs and J. Freund (*Ber.*, 1941, **74**, [*B*], 1085—1088).—$SnCl_2$ in conc. HCl at 100° reduces 3-nitro-4-amino- to 3 : 4-*diamino-2-methylquinoline*, m.p. 226—227° (*hydrochloride*, $+H_2O$, m.p. 317—318°; picrate, m.p. 227—228°), which with HNO_2 gives a triazole derivative (*hydrochloride*, m.p. 316°; picrate, darkens >220°, decomp. 252°). Passing HCl gas into 4-chloro-3-nitro-2-methylquinoline and $SnCl_2$ in AcOH gives exothermally 3-amino-2-methylquinoline, m.p. 160—161° (lit., 159—160°) (gives 3-chloro-2-methylquinoline by a diazo-reaction), and a small amount of 4-chloro-3-amino-2-methylquinoline (*hydrochloride*, m.p. 150° after sintering; picrate, darkens from 200°, decomp. ~220°), which is the sole product of reduction by $Fe(OH)_2$–aq. NH_3–MeOH at 90°. The structure of the product from N_2H_4 and 4-chloro-2-methylquinoline remains obscure (cf. A., 1935, 989). R. S. C.

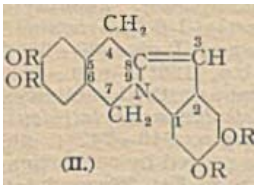
Heterocyclic ketones. II. Alkylation. E. I. Elkina and M. M. Schemjakin. **III. Chlorination by means of oxalyl chloride.** M. M. Schemjakin and E. I. Elkina (*J. Gen. Chem. Russ.*, 1943, **13**, 164—168, 169—174).—II. The K_2 salt of 6-hydroxynicotinic acid with Pr$^\alpha$I in Pr$^\alpha$OH (1 hr. at 180°) yields a mixture of N-*propyl-2-pyridone-5-carboxylic acid* (**I**), m.p. 141—142°, 6-n-*propoxynicotinic acid*, m.p. 116—117°, and the *Pr*$^\alpha$ ester of (**I**), b.p. 147—149°/4 mm.

III. *N*-Methyl-2-quinolone and $(COCl)_2$ in Et_2O yield 2 : 2-*dichloro-1-methyl-1 : 2-dihydroquinoline*, whilst with (**I**) the product is 2 : 2-*dichloro-1-propyl-1 : 2-dihydropyridine-5-carboxylic acid*; these Cl_2-derivatives rapidly decompose on exposure to the atm. 1-Hydroxy-: 8-dimethoxy-3-acetyl*iso*quinoline and $(COCl)_2$ in Et_2O give 1-*chloro-7 : 8-dimethoxy-3-acetyl*isoquinoline, m.p. 145—146°, whilst with PCl_5 the product is 1-*chloro-7 : 8-dimethoxy-3-α-chlorovinyl*isoquinoline, m.p. 116—117°. 2-Pyridone and $(COCl)_2$ yield a *substance*, $C_{10}H_{10}ON_2Cl_2$, m.p. 137—138°. R. T.

Syntheses by means of sodamide. O. Eisleb (*Ber.*, 1941, **74**, [*B*], 1433—1450).—*tert.* Halogenoalkyl-amines or -amides do not react with $NaNH_2$ or $NaNH_2$–NH_3 at 100°. $NaNH_2$ is thus a very effective reagent for introducing aminoalkyl groups into substances which contain H replaceable by Na. Further, use of NR($[CH_2]_2$·Cl)$_2$ and substances containing activated CH_2 leads to di-condensation with formation of 4-substituted piperidine derivatives. X($[CH_2]_2$·Cl)$_2$ (X = S or O) react similarly. The best technique is to add $NaNH_2$, ground in a warm, dry mortar, gradually to the reactants in PhMe, usually at 40—60°, raised later to ~100°; condensations below are thus effected, successive temp. being noted in parentheses. $NEt_2·[CH_2]_2$·Cl (**I**) and COPh·CH_2Ph give (45—50°, b.p.) *γ-diethylamino-α-phenyl-n-butyrophenone* (80%), b.p. 192—193°/4 mm., the hydrochloride, m.p. 148°, of which has spasmolytic activity. $CH_2Ph·SO_2Ph$ and (**I**) give (50—55°, 90—95°) *Ph γ-diethylamino-α-phenyl-n-propyl sulphone*, m.p. 39—40°, b.p. 210°/3 mm. (hydrochloride, m.p. 139—140°, neutral in H_2O). CH_2Ph_2 and (**I**) give (b.p.) only 14% of *γγ-diphenyl-n-propyldiethylamine*, b.p. 170—175°/4 mm., the hydrochloride, m.p. 143—144°, of which has local anæsthetic and spasmolytic activity. Indene and (**I**) give (in C_6H_6; 40—50°, 80°) *3-β-diethylaminoethylindene*, b.p. 140°/4 mm., the hydrochloride, m.p. 156—159°, of which has local anæsthetic activity. Fluorene and (**I**) give (60°; 100°) *9-β-diethylaminoethylfluorene*, b.p. 192—210°/4 mm., the hydrochloride, m.p. 217—218°, of which is weakly acid in H_2O and has local anæsthetic activity. $NHPh_2$ and (**I**) give (60°, 90—100°) *NN-diphenyl-N′N′-diethylethylenediamine* (81%; <40% in absence of $NaNH_2$), b.p. 173—174°/4 mm., the monohydrochloride, m.p. 169—170°, and N′-methobromide, m.p. 173°, of which have local anæsthetic activity. Pyrrole and (**I**) give (in C_6H_6; 40—50°, 80°) *1-β-diethylaminoethylpyrrole* (~66%), b.p. 223—225°/760 mm., 80°/4 mm. (hydrochloride, m.p. 113—114°, has no pharmacological action; ethylethosulphate, m.p. 131—132°). Pyrrole does not react with (**I**) in presence of NaOEt–EtOH, but tetraiodopyrrole at 30—35° and then 40° thus gives 2 : 3 : 4 : 5-tetraiodo-1-β-diethylaminoethylpyrrole, sinters 114°, m.p. 120° (decomp.) (hydrochloride; nitrate; phosphate). 2-Methylindole and (**I**) (in C_6H_6; 40—50°, 80°) give *2-methyl-1-β-diethylaminoethylindole* (80%), b.p. 156°/4 mm. Carbazole and (**I**) give (85—90°; 100°) *9-β-diethylaminoethylcarbazole* (94%), b.p. 196°/3 mm., the phosphate, m.p. 151—155°, of which has local anæsthetic activity. Acridone and (**I**) give (120—130°) *10-β-diethylaminoethylacridone* (97%), m.p. 112—113° (hydrochloride, decomp. 246—247°; no oxime or hydrazone), the structure of which is proved by conversion by Na–EtOH into 10-β-diethylaminoethyl-, m.p. 58—59°, and by MgPhBr into 5-hydroxy-5-phenyl-10-β-diethylaminoethyl-acridan, m.p. 151—153° (and the derived acridinium chloride hydrochloride). $CH_2Ph·CN$ and (**I**) give (in C_6H_6; <40°, 75—80°) *γ-diethylamino-α-phenyl-n-butyronitrile* (~60%), b.p. 132°/3 mm. *n*-C_6H_{13}·CHPh·CN and (**I**) give *α-phenyl-α-β′-diethylaminoethyl-n-octonitrile* (>75%), b.p. 180—185°/4 mm. $CH_2Ph·CHPh·CN$ and 1-β-chloroethylpiperidine give (45—50°, 95—105°) *γ-piperidino-α-phenyl-α-benzyl-n-butyronitrile*, m.p. 93°, b.p. 203°/3 mm. (hydrochloride, m.p. 215°), and another base, b.p. 200—210°/3 mm. $MeSO_2·NEt_2$ and (**I**) give (80°, 100—105°) *γ-diethylaminopropanesulphondiethylamide*, b.p. 185°/20 mm. (hydrochloride, m.p. 120—121°). NR($[CH_2]_2$·Cl)$_2$,HCl are prepared from NR($[CH_2]_2$·OH)$_2$ by $SOCl_2$ and are stable, but the free bases are unstable and are prepared therefrom *in situ* just before use. $CH_2Ph·CN$ and NMe($[CH_2]_2$·Cl)$_2$ (**II**), b.p. 71°/9 mm., give (30—40°, b.p.) *4-phenyl-1-methylpiperidine-4-nitrile* (**III**) (66%), m.p. 53°, b.p. 148°/4·5 mm. (hydrochloride, m.p. 221—222°, sublimes at 6 mm.), hydrolysed by KOH–MeOH–H_2O at 160—170° to the 4-carboxylic acid (**IV**), $+H_2O$, m.p. 299° (decomp.) [neutral in H_2O; chloride hydrochloride, m.p. indefinite, >150° (decomp.)], which at 340° slowly gives *4-phenyl-1-methylpiperidine*, b.p. 255—260°/760 mm., 130°/15 mm. (hydrochloride, m.p. 196—197°; picrate, decomp. 236—237°; picrolonate, m.p. 221°). Treating (**III**) with 80% (wt.) H_2SO_4 at 130—150° and then gradually adding EtOH at 103—108° (temp. in liquid) gives the *Et* ester (~95%), m.p. 30°, b.p. 155°/5 mm. (*hydrochloride*, m.p. 187—188°; picrate, m.p. 189—190°; H_2 citrate, decomp. >206°), of (**IV**). p-*Toluenesulphondi-β-hydroxyethylamide* {prep. from *p*-$C_6H_4Me·SO_2Cl$ and NH($[CH_2]_2$·OH)$_2$ in 2N-Na_2CO_3 at 65—70° and then 95°}, m.p. 100—101°, with $SOCl_2$ at 90—95° and then 130° yields p-*toluenesulphondi-β-chloroethylamide*, m.p. 48—49°, which with $CH_2Ph·CN$ gives (40—45°, b.p.) *p-toluenesulphon-4-phenylpiperidide-4′-nitrile* (37%), m.p. 200—201°, converted by 75% H_2SO_4 at 140—150° and then EtOH at 110° as above into *Et 4-phenylpiperidide-4-carboxylate* (~85%), m.p. 36—37°, b.p. 155°/3·5 mm. [hydrochloride (**V**), m.p. 133—134°; picrate, m.p. 157—158°]. $CH_2Ph·N($$[CH_2]_2$·Cl)$_2$, b.p. ~126—127°/1 mm. (hydrochloride, m.p. 149°), and $CH_2Ph·CN$ give (35—50°, b.p.) *4-phenyl-1-benzylpiperidine-4-nitrile*, m.p. 75—76° (hydrochloride, m.p. 259—260°), and thence (70% H_2SO_4) the 4-carboxylic acid, decomp. 288° (*Et* ester, m.p. 73—74°); the derived Et ester hydrochloride, decomp. 235—238°, with H_2–Pd-black in EtOH at 40—50° gives (**V**). O($[CH_2]_2$·Cl)$_2$ and $CH_2Ph·CN$ give (40—50°, 100°) *4-phenyltetrahydropyran-4-nitrile* (49%), m.p. 49—50°, b.p. 147—148°/5 mm., hydrolysed by 66% H_2SO_4 at 100° to the 4-carboxylamide, m.p. 216—218° (which has sedative action), and by hot KOH–MeOH to the *4-carboxylic acid*, m.p. 129—130° [chloride, m.p. 53—54°, b.p. 140°/3 mm.; *β-diethylaminoethyl* ester, an oil (hydrochloride, m.p. 181°, spasmolytic)]. $CH_2Ph·CN$ and S($[CH_2]_2$·Cl)$_2$ give (40—45°, b.p.) *4-phenylpentamethylene sulphide-4-nitrile* (47%), m.p. 56—57°, b.p. 175°/6 mm., and thence by 80% H_2SO_4 at 72° the 4-carboxylamide (**VI**), m.p. 158—159°, and *4-carboxylic acid* (better obtained by KOH–MeOH at 190—200°), m.p. 157—158° (1 : 1-dioxide, m.p. 215°); the 1 : 1-dioxide, m.p. 237—238°, of (**VI**) has sedative action. 1-Methyloxindole and (**II**) give (35—45°, b.p.) 1 : 1′-*dimethylpiperid-*

ine-4-spiro-3′-*oxindole* (51%), m.p. 104—106° (hydrochloride, m.p. 245—246°). Fluorene and (**II**) give (100—105°, 140°) 1-*methylpiperidine*-4-spiro-9′-*fluorene*, m.p. 113·5—114·5° (hydrochloride, m.p. 274—275°, has local anæsthetic action; phosphate, m.p. 244—246°). $MeSO_2{\cdot}NEt_2$ and (**II**) give (80°, 100—105°) 1-*methylpiperidine*-4-*sulphondiethylamide*, m.p. 32°, b.p. 138°/3 mm. (hydrochloride, m.p. 183—185°). $PhMeSO_3$ and (**II**) give (90—95°, 105—110°) 1-*methyl*-4-*piperidyl Ph sulphone*, m.p. 115°, b.p. 182—192°/3 mm. (hydrochloride, m.p. 228—229°). $CH_2Ph{\cdot}SO_2Ph$ and (**II**) give (45—50°, 95—100°) 4-*phenyl*-1-*methyl*-4-*piperidyl Ph sulphone*, m.p. 165° [hydrochloride, m.p. 251° (decomp.)]. Attempts to alkylate $CH_2Ph{\cdot}CO{\cdot}NR_2$ (R = Et or Ph) failed, as did attempts to prepare piperidine derivatives from $CH_2Ph{\cdot}COPh$ or CH_2Ph_2 by (**II**). R. S. C.

Synthesis of nitrogenous hetero-rings. XXIV. Synthesis of dibenzindolizine derivatives. I. Synthesis of 4′ : 5′ : 4″ : 5″-tetramethoxy-3 : 4 : 7 : 8-tetrahydro-1 : 2 : 5 : 6-dibenzindolizine. S. Sugasawa and K. Kodama (*Ber.*, 1941, **74**, [*B*], 1237—1241).—6 : 7 : 3′ : 4′-Tetramethoxy-3-benzyl-3 : 4-dihydro*iso*quinoline methylmethosulphate and H_2–PtO_2 in EtOH give 6 : 7 : 3′ : 4′-*tetramethoxy*-3-*benzyl*-1-*methyl*-1 : 2 : 3 : 4-*tetrahydroisoquinoline*, m.p. 99°, converted by HI (*d* 1·7) at 150° into the corresponding $(OH)_4$-compound (*tetra-acetate*, m.p. 133—135°), the hydriodide of which with KOAc, then chloranil in EtOH, and finally HCl gives 3′ : 4′ : 3″ : 4″-tetrahydroxy-9-methyl-3 : 4 : 7 : 8-tetrahydroindolizinium chloride (**I**) (cf. Robinson *et al.*, A., 1932, 527). Me_2SO_4–33% KOH–H_2 and then KI converts (**I**) into the *Me*$_3$ *ether iodide*, decomp. 248—249°, which at 215—220° (the crude salt decomposes) gives 3 : 4′ : 3″ : 4″-*tetramethoxy*-3 : 4 : 7 : 8-*tetrahydro*-, m.p. 146—147° (decomp.), dehydrogenated by Pt-black and air in boiling EtOH to 3′ : 4′ : 3″ : 4″-*tetramethoxy*-4 : 7-*dihydro*-1 : 2 : 5 : 6-*dibenzindolizine* [(**II**) R = Me], m.p. 193—194° (purple-red Ehrlich reaction). With boiling Ac_2O and a few drops of C_5H_5N, (**I**) gives 3′ : 4′ : 3″ : 4″-*tetra-acetoxy*-4 : 7-*dihydro*-1 : 2 : 5 : 6-*dibenzindolizine* [(**II**) R = Ac], m.p. 198—200°, unaffected by air–Pt-black in EtOH.



(II.)

R. S. C.

***p*-Nitrophenylmethylpyrazolone.** T. Iseki, T. Sugiura, S. Yasunaga, and M. Nakasima (*Ber.*, 1941, **74**, [*B*], 1420—1424).—Picrolonic acid (**I**) and conc. HNO_3 (*d* 1·45) give 4 : 4-*dinitro*-1-p-*nitrophenyl*-3-*methyl*-5-*pyrazolone* (**II**) (almost 100%), m.p. 204°, which is unstable. In NaOH, (**II**) gives CO_2 and as.-*dinitroacetone*-p-*nitrophenylhydrazone*, m.p. 147°. In MeOH, (**II**) gives *nitropyrazole-blue* [*di*-(5-*keto*-1-p-*nitrophenyl*-3-*methyl*-4-*pyrazolidene*)] (**III**) (96%), decomp. 255°, which is also obtained from 1-*p*-nitrophenyl-3-methyl-5-pyrazolone by $NHPh{\cdot}NH_2$ and then $FeCl_3$. Heating (**I**) at 124—125° (10 min.) gives 4 : 4-*dihydroxy*-1-p-*nitrophenyl*-3-*methyl*-5-*pyrazolone* (**IV**), yellow, m.p. 185° [obtained as a by-product (1·7%) during the above prep. of (**III**)], with small amounts of (**III**) and an orange-red substance, m.p. 199—200°. With $NHPh{\cdot}NH_2$, (**IV**) in boiling AcOH gives 1-p-*nitrophenyl*-3-*methyl*-4 : 5-*diketopyrazoline*-4-*phenylhydrazone*, m.p. 242°, and, when repeatedly crystallised from MeOH, gives 4-*hydroxy*-5-*methoxy*-1-p-*nitrophenyl*-3-*methyl*-5-*pyrazolone*, m.p. 192—193° (red in alkali). (**IV**) gives a red colour in dil. NaOH and hydrolysis occurs yielding *αβ-diketo*-n-*butyric acid*-*β*-p-*nitrophenylhydrazone* (90%), m.p. 175—176°. R. S. C.

Pyridyl and pyrazole acetamides.—See B., 1944, II, 101.

Action of nitric acid on ethyl *iso*dehydroacetate.—See A., 1944, II, 179.

***p*-Nitrobenz-*β*-4-iminazylethylamide.**—See B., 1944, III, 101.

Action of phosphorus pentasulphide on barbituric acids. H. C. Carrington (*J.C.S.*, 1944, 124—126).—When barbituric acids containing two hydrocarbon residues in the 5-position react with P_2S_5, one, two, or three of the O of the barbituric acid ring may be replaced by S according to the reaction conditions and the nature of the substituents (cf. Henze *et al.*, A., 1943, II, 339). 5 : 5-Diethylbarbituric acid, P_2S_5, and K_2S in xylene give 5 : 5-*diethyl*-2 : 4-*di*-, m.p. 205—206°, and -2 : 4 : 6-*tri*-*thiobarbituric acid* (**I**), m.p. 192—193°, also obtained from the -2-thio-acid. Aq. NH_3 and (**I**) afford 6-*imino*-5 : 5-*diethyl*-2 : 4-*dithiobarbituric acid*, decomp. at 230°, whilst (**I**) with Me_2SO_4–NaOH gives the 6-*methylthio*-*acid*, m.p. 130°. The following are also described: 5-*ethyl*-5-n-*propyl*-2 : 4-*di*-, m.p. 180°, and -2 : 4 : 6-*tri*-, m.p. 177°, -5-iso*propyl*-2 : 4-*di*-, m.p. 173°, 5 : 5-*di*-n-*propyl*-2 : 4-*di*-, m.p. 189°, and -2 : 4 : 6-*tri*-, m.p. 205—206°, 5-*ethyl*-5-n-*butyl*-2 : 4-*di*-, m.p. 127°, 5-*ethyl*-5-iso*butyl*-2 : 4-*di*-, m.p. 190°, and -2 : 4 : 6-*tri*-, m.p. 143°, 5-*ethyl*-5-*β*-*methylbutyl*-2 : 4-*di*-, m.p. 158°, 5 : 5-*di*-n-*butyl*-2 : 4-*di*-, m.p. 125°, and -2 : 4 : 6-*tri*-, m.p. 164°, 5-*phenyl*-5-*ethyl*-2 : 4-*di*-, m.p. 246°, and -2 : 4 : 6-*tri*-, m.p. 162—164°, and 5-*benzyl*-5-*ethyl*-2-*mono*-, m.p. 180°, and -2 : 4-*di*-*thiobarbituric acid*, m.p. 160°. F. R. S.

Thiobarbituric acids.—See B., 1944, III, 101.

Formation of pyrimidine rings. Z. Foldi and A. Salamon (*Ber.*, 1941, **74**, [*B*], 1125—1128).—$NH_2{\cdot}CMe{:}N{\cdot}CH{:}C(CN){\cdot}CO_2Et$ (**I**) with HCl–EtOH at 0° gives the imino-ether and thence by hot NaOEt–EtOH Et 4-amino-2-methylpyrimidine-5-carboxylate (**II**), m.p. 122°, converted by aq. NH_3 (*d* 0·91) at room temp. into the derived amide, m.p. 260—261° (*hydrochloride*), and by 2·5% NaOH at 90° into the derived *acid*, m.p. 275° (*hydrazide*, m.p. 220°). If (**I**) is freed from traces of alkali by AcOH and then heated in boiling H_2O, (**II**) is formed, and the picrate, m.p. 170—175°, of (**II**) is obtained when the picrate, m.p. 140—144°, of (**I**) is melted. The effect of alkali on the direction of ring-closure is noted (cf. Todd *et al.*, A., 1937, 216). R. S. C.

Ethyl esters of 2-keto- and 2-thio-1 : 2 : 3 : 4-tetrahydro-5-pyrimidinecarboxylic acids. D. W. McKinstry and (Miss) E. H. Reading (*J. Franklin Inst.*, 1944, **237**, 203—205).—$CO(NH_2)_2$ (1 mol.), $CH_2Ac{\cdot}CO_2Et$ (1·5 mols.), and a substituted PhCHO (1 mol.) boiled in EtOH (modified Biginelli condensation) give Et 2-*keto*-4-*R*-6-*methyl*-1 : 2 : 3 : 4-*tetrahydropyrimidine*-5-*carboxylates*, R depending on the aryl substituent. R = 2-*chlorophenyl*, m.p. 214°, 5-*chloro*-2-*hydroxyphenyl*, m.p. 203°, 3 : 4-*diethoxyphenyl*, m.p. 165°, 4-*dimethylaminophenyl*, m.p. 231°, 4-*diethylaminophenyl*, m.p. 199°. With $CS(NH_2)_2$ the following *Et* 2-*thion*-4-*R*-6-*methyl*-1 : 2 : 3 : 4-*tetrahydropyrimidine*-5-*carboxylates* are obtained: R = 3 : 4-*dimethoxyphenyl*, m.p. 231°, 3 : 4-*diethoxyphenyl*, m.p. 125°, 4-*dimethylaminophenyl*, m.p. 197°, and 4-*diethylaminophenyl*, m.p. 200°. D. G.

Pyrazine–water azeotrope.—See A., 1944, I, 150.

Reactions of *NN*′-diacetyltetrahydro-4 : 4′-dipyridyl. B. Emmert and A. Wolpert (*Ber.*, 1941, **74**, [*B*], 1015—1018).—Di-1-acetyl-1 : 4-dihydro-4-pyridyl (**I**) (modified prep.; cf. Dimroth *et al.*, A., 1922, i, 48) in Ac_2O–CO_2 at 100° gives C_5H_5N, 4-ethylpyridine (**II**), and a little di-4-pyridyl, but in boiling MeOH–CO_2 gives C_5H_5N, (**II**), and 4-acetylpyridine [oxime, m.p. 157·5—158° (lit., 142°)]. With NH_2OH in boiling MeOH–CO_2 (**I**) gives 1-*acetyl*-4-*α*-*oximinoethyl*-1 : 4-*dihydropyridine*, m.p. 121—122° (rapid heating), and some C_5H_5N. In presence of Pd-black in EtOH, (**I**) absorbs ~4 H_2 to yield *di*-1-*acetyl*-4-*piperidyl*, m.p. 174°. Reaction mechanisms are discussed. R. S. C.

Pyridylquinolines etc.—See B., 1944, II, 102.

Synthesis of dimethoxyquinazolones. V. M. Rodionov and A. M. Fedorova (*J. Gen. Chem. Russ.*, 1943, **13**, 249—252).—2-Amino-3 : 4-dimethoxybenzoic acid, heated with Ac_2O, yields 6-*keto*-3′ : 4′-*dimethoxy*-2-*methylbenzo*-2 : 1-4 : 5-*oxazine* (**I**), m.p. 165—168°, converted by recrystallising from AcOH into 2-*acetamido*-3 : 4-*dimethoxybenzoic acid*, m.p. 194—195°, and by aq. NH_3 into 7 : 8-*dimethoxy*-2-*methyl*-4-*quinazolone* (*hydrochloride*, m.p. 226—228°). 6-Amino-2 : 3-dimethoxybenzoic acid similarly yields 6-keto-3′ : 4′-dimethoxy-2-methylbenzo-1 : 2-4 : 5-oxazine, but this reacts differently with aq. NH_3, giving 2-acetamido-5 : 6-dimethoxybenzamide. *β*-Amino-*ε*-diethylaminopentane and (**I**) (2—3 hr. at 120—130°) afford 7 : 8-*dimethoxy*-2-*methyl*-3-(5-*diethylamino*-*α*-*methylbutyl*)-4-*quinazolone* (*trihydrochloride*, m.p. 171—173°). R. T.

***iso*Oxindigo.** P. Chovin (*Compt. rend.*, 1942, **215**, 466—468).—Condensation of *o*-$OH{\cdot}C_6H_4{\cdot}CH_2{\cdot}CO_2H$ with *o*-$OH{\cdot}C_6H_4{\cdot}CO{\cdot}CO_2H$ by PBr_3 gives an orange substance (**I**), converted by KOH–EtOH followed by HCl into a yellow *compound* (**II**), $C_{16}H_8O_3$, m.p. 305°. The constitution of the two isomerides cannot be elucidated by considerations of colour. (**I**) gives a difficultly purified ozonide (**III**), transformed by hydrolysis or pyrolysis into *o*-$OH{\cdot}C_6H_4{\cdot}CO_2H$ and *o*-$OH{\cdot}C_6H_4{\cdot}CO{\cdot}CO_2H$ or its lactone, whereas (**II**) affords a colourless *substance*, $C_{16}H_8O_6$, m.p. 269°, which behaves like (**III**) when pyrolysed. Improvement in the yield of (**I**) by the substitution of the lactones for the acids indicates for it the *iso*indigoid structure and this view is strengthened by the exclusive formation of (**I**) in 50% yield from 2-coumaranone. (**II**) is thus probably the dibenzonaphthyrone. H. W.

Action of oxidising agents on 5-keto-3-thion-6-benzyl-1 : 2 : 4-triazine. E. Cattelain (*Compt. rend.*, 1942, **215**, 257—259).—5-Keto-3-thion-6-benzyl-1 : 2 : 4-triazine (**I**) is converted by I in neutral solution into *di*-5-*keto*-6-*benzyl*-1 : 2 : 4-*triazinyl* 3 : 3′-*disulphide*, m.p. 173°, which does not reduce Nessler's reagent or Cu^{II} salts but is transformed into (**I**) by $(NH_4)_2S$ or $NaHSO_3$. It gives a green Cu^{II} (**II**) and a yellow Cu^{I} (**III**) salt, both insol. in H_2O. When freshly prepared it liberates I from KI in acid solution. In presence of phenolphthalein it can be titrated as a di-acid. It is converted by Na–Hg into *α*-*thiosemicarbazido*-*β*-*phenylpropionic acid*. With excess of I in alkaline solution (**I**) gives 3 : 5-*diketo*-6-*benzyl*-1 : 2 : 4-*triazine*. (**I**) is transformed by $CuSO_4$ according to the relative proportions into a mixture of the Cu compound of (**I**) and (**III**), a mixture of (**II**) and (**III**), or exclusively (**III**). H. W.

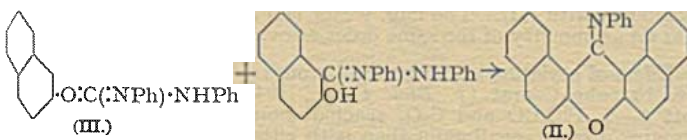
Invert soaps. VII. Tetrazolium salts. R. Kuhn and D. Jerchel [with, in parts, E. F. Moller, M. von Czernucki-Hrebeljanowitsch, and R. Brill] (*Ber.*, 1941, **74**, [*B*], 941—948).—$NHPh{\cdot}N{:}CH{\cdot}CO_2Et$, m.p. 133° (lit., 131°), is best obtained by exothermal interaction of $NHPh{\cdot}NH_2$ with $CO_2Et{\cdot}CH(OH){\cdot}OEt$. Formazans, $NR'{:}N{\cdot}CR'{:}N{\cdot}NHR''$, are obtained by treating $CHR'{:}N{\cdot}NHR''$ with RN_2Cl and NaOAc in EtOH; they are tautomeric with $NR''{:}N{\cdot}CR'{:}N{\cdot}NHR$ (cf. von Pechmann, A., 1894, i, 456; Busch

et al., A., 1931, 1156), since the pairs, R = Ph, R'' = *p*-NO_2·C_6H_4 or vice versa, and R = Ph, R'' = *p*-C_6H_4Br or vice versa (R' = *n*-$C_{11}H_{23}$ in both cases), are identical when prepared from any possible set of components. Formazans are best (72—83%) oxidised to tetrazolium salts by $Pb(OAc)_4$. Thus are prepared: *C*-carbethoxy-*NN'*-diphenylformazan, m.p. 110° (lit., 114·5°); NN'-*diphenyl*-C-n-*hexyl*- (**I**), m.p. 76°, and -C-n-*undecyl*-, m.p. 61°, -*formazan*; N-*phenyl*-N'-p-*nitrophenyl*- (**II**), m.p. 108—109°, -N'-p-*bromophenyl*-, m.p. 53°, and -N'-α-*naphthyl*-, m.p. 60°, -C-n-*undecylformazan*; 2 : 3-*diphenyl*-5-*methyl*-, decomp. 271°, -5-n-*hexyl*- (**III**), decomp. 220°, and -5-n-*undecyl*- (**IV**), m.p. 141°, -*tetrazolium chloride*; 2 : 3 : 5-triphenyl-, decomp. 263° (lit., m.p. 243°), and 5-carboxy-2 : 3-diphenyl-, decomp. 198—200° (lit., 195—198°), -tetrazolium chloride; 2-*phenyl*-3-p-*bromophenyl*- (**V**), m.p. ~60°, and -3-α-*naphthyl*- (**VI**), a glass, -5-n-*undecyltetrazolium chloride*. M.p. are taken on a microscope stage. Absorption spectra (detailed) of (**I**) and (**III**) differ greatly. (**II**) gives a deep green $Cu^{II}_{0·5}$ derivative, m.p. 131°, indicating that the tautomerism of formazans depends on chelation. The tetrazolium salts ppt. egg-albumin at pH > the isoelectric point. Drop nos. of 1% solutions are (**III**) 46·4 and (**IV**) 75·7. Bacteriostatic properties of (**IV**)—(**VI**) against lactic acid bacteria approx. equal those of *n*-$C_{12}H_{25}$·NMe_2Br·CH_2Ph; those against *Staph.*, paratyphus, *B. coli*, diphtheria and Friedlander bacilli are ≪ those of benztriazolium salts (A., 1942, II, 112).

R. S. C.

Identity of " euglenarhodone " with astacene.—See A., 1944, III, 444.

Internal rearrangements in the aromatic series. III. Arylation and alkylation of aryl substituted carbamides. G. I. Gerschzon (*J. Gen. Chem. Russ.*, 1943, **13**, 136—144).—β-$C_{10}H_7$·OH (**I**) with NHPh·CO·NPhEt or NHPh·CO_2Me at 240—250° for 4 hr. yields 2 : 3 : 5 : 6-di-2′ : 1′-naphtha-1 : 4-pyrone 4-anil (**II**). (**I**) and NHPh·CO·NH_2 (6 hr. at 245°) give 2-$C_{10}H_7$·NHPh, in 54% yield. CO(NPhEt)$_2$ does not react with (**I**), even at 300°. The process of formation of (**II**) is, on the basis of the above results, and of those of Dziewonski *et al.* (cf. A., 1933, 833), presented as: (**I**) + CO(NHPh)$_2$ → NHPh·C(O·$C_{10}H_7$):NPh (**III**). Part of (**III**) undergoes intramol. rearrangement to the anil of 1-phenylcarbamyl-2-naphthol, which condenses with (**III**) as follows:



R. T.

Thiazoles. I. Condensation of αδ-dichloro-γ-valerolactone with thioamides. H. Beyer (*Ber.*, 1941, **74**, [*B*], 1100—1104).—δ-Chloro-α-acetyl-γ-valerolactone (1) and SO_2Cl_2 (1 mol.) at 0° (exothermally) and then 100° give *αδ-dichloro-α-acetyl-γ-valerolactone* (**I**), b.p. 130—131°/0·3 mm., which in dil. HCl at 100° gives CH_2Cl·CH(OH)·CH_2·CHCl·COMe (**II**), which spontaneously yields mostly 4-*chloro*-5-*methyl*-2-*chloromethyl*-2 : 3-*dihydrofuran*. When (**I**) is heated with $CS(NH_2)_2$ in 4N-HCl at 100°, the intermediate (**II**) condenses to yield, with loss of HCl, 2-*amino*-4-*methyl*-5-*βγ-epoxy-n-propylthiazole*, sinters 145°, m.p. 150—152° (clear at 153°) (*picrate*, sinters 172°, m.p. 175—176°) (and some dihydrofuran derivative, b.p. 70—75°/0·1 mm.), which, when made acid to Congo-red by HCl in MeOH, yields 2-*amino*-4-*methyl*-5-γ-*chloro*-β-*hydroxy*-n-*propylthiazole*, m.p. 144—146° (*picrate*, sinters 185°, m.p. 190—192°). With MeCS·NH_2 or PhCS·NH_2, (**I**) in 4N-HCl at 100° similarly yields 2 : 4-dimethyl-5-*βγ*-epoxy-*n*-propylthiazole (*picrate*, m.p.136—137°) and 2-phenyl-4-methyl-5-γ-chloro-β-hydroxy-*n*-propylthiazole (*hydrochloride*, m.p. 198—199° (decomp.)], respectively. R. S. C.

Benzthiazole. E. Ochiai and T. Nishizawa (*Ber.*, 1941, **74**, [*B*], 1407—1415).—Although cyclic S is generally equiv. to cyclic CH:CH, the reactivity of the C_6H_4 ring of benzthiazole differs from that of the C_6H_4 ring of quinoline. 6-Hydroxy-2-methylbenzthiazole (**I**) with CH_2:CH·CH_2Br and K_2CO_3 in boiling abs. EtOH gives the *allyl ether* (**II**) (85%), b.p. 130—140° (bath)/0·03 mm. (*picrate*, m.p. 152°), which at 240—250° (10 min.) gives a mixture (~20 : 1) of 6-*hydroxy*-2-*methyl*-7- (**III**), m.p. 133—135°, resolidifies, remelts 141° (*picrate*, m.p. 125—126°), and -5-*allylbenzthiazole* (**IV**), m.p. 188° (*picrate*, decomp. 216—219°), with 4% of unchanged (**II**). (**III**) and (**IV**) give allyl ethers, b.p. ~180° (bath)/0·1 mm. (*picrates*, m.p. 115—116° and 161—163°, respectively), converted at 235—250° into 6-*hydroxy*-2-*methyl*-5 : 7-*diallylbenzthiazole* (**V**), m.p. 148°, the allyl ether (*picrate*, m.p. 92°) of which is stable at 240°. PhN$_2$Cl does not couple with (**I**) in aq. AcOH but in NaOH gives the *PhN$_2$*-derivative (82%), m.p. 119°. *p*-NO_2·C_6H_4·N_2Cl (**VI**) and (**I**) in aq. AcOH or NaOH give the *p*-NO_2·C_6H_4·N_2-derivative (90—95%), m.p. 224—225°. PhN$_2$Cl does not couple with (**III**) in acid or alkali, but (**VI**) in alkali (not acid) gives a little 6-*hydroxy*-5-p-*nitrobenzeneazo*-2-*methyl*-7-*allylbenzthiazole*, m.p. 203°. (**IV**) couples with (**VI**) in acid or alkali giving 6-*hydroxy*-7-p-*nitrobenzeneazo*-2-*methyl*-5-*allylbenzthiazole*, m.p. 147°. (**V**) and (**VI**) do not react in acid or alkali. R. S. C.

Constitution of the so-called carbothialdines and the preparation of some homologous compounds. A. D. Ainley, W. H. Davies, H. Gudgeon, J. C. Harland, and W. A. Sexton (*J.C.S.*, 1944, 147—152).—Consideration of methods of formation leads to structure S<CHR′·NH / CS—NR>CHR′ [(**I**), R = H, R′ = Me] for " carbothialdine " (or " thiuram carbomethyl ") and to (**I**) (R = Me, R′ = H) for " dimethylformocarbothialdine " which is identical with " 2 : 4-dimethyl-2-methylenecarbothialdine " Absorption spectra are in accord with the proposed formulæ and the names should be 2-thio-4 : 6- and -3 : 5-dimethyltetrahydro-1 : 3 : 5-thiadiazine, respectively. NH_2Ph, CS_2, and H_2O with aq. NH_2Me give *2-thio-3-phenyl-5-methyltetrahydro-1 : 3 : 5-thiadiazine*, m.p. 148°. By treatment of the Ba salt of the aryldithiocarbamic acid with the sulphate of the aliphatic amine, followed by CH_2O, the following have been prepared: *2-thio*-3-α-*naphthyl*-, m.p 159—160°, -3-(p-*chlorophenyl*)-, m.p. 139—140°, -3-(p-*anisyl*)-, m.p. 160—161°, -3-(p-*hydroxyphenyl*)-, m.p. 163—164°, 3-(3′-*chloro*-4′-*hydroxyphenyl*)-, m.p. 146°, and -3-(p-*dimethylaminophenyl*)-5-*methyltetrahydro*-, m.p. 168—169°; and *2-thio*-3-*phenyl*-5-(β-*diethylamino*)-, m.p. 103—104° (with some *OH·CH_2* derivative of 2-anilino-4 : 5-dihydrothiazole, m.p. 165°), and -5-(β-*hydroxyethyl*)-*tetrahydro*-1 : 3 : 5-*thiadiazine*, m.p. 136°; and p-*diethylaminophenylammonium* p-*diethylaminophenyldithiocarbamate*, m.p. 97—99°. F. R. S.

VII.—ALKALOIDS.

Hydrazides of dihydro-lysergic and -*iso*lysergic acids.—See B., 1944, III, 102.

Chemical study of *Fritillaria raddeana*, RGL. A. Sadikov and G. Lazurevski (*J. Gen. Chem. Russ.*, 1943, **13**, 159—163).—The dry bulbs contain carbohydrates 60·5 (monosaccharides 2·4, disaccharides 6·2, starch 41·3, cellulose 7·8, and hemicellulose 2·8%), resins 4, and an alkaloid *raddeanine* (**I**), $C_{21}H_{35}O_2N$, m.p. 255—257°, 0·7%. The carbohydrates may be utilised as fodder, or as a nutrient medium for yeast. The *perchlorate*, m.p. 204—205°, *hydrochloride*, m.p. 167—168°, *aurochloride*, m.p. 130—132°, *methiodide*, m.p. 248—250°, and *Bz* derivative, m.p. 235—236°, of (**I**) are described. (**I**) is not affected by treatment with KOH–EtOH (5 hr. at the b.p.).

R. T.

Aconite alkaloids. XIII. Isolation of pimanthrene from dehydrogenation products of staphisine. XIV. Oxidation of the hydrocarbon from dehydrogenation of atisine. L. C. Craig and W. A. Jacobs (*J. Biol. Chem.*, 1944, **152**, 645—650, 651—657; cf. A., 1943, II, 210).—XIII. Commercial abietic acid (probably contains some *d*-pimaric acid) is dehydrogenated by Se at 340° (in N_2) for 2 hr. to give, after chromatographic separation, retene and some pimanthrene, m.p. 84—85° (picrate, m.p. 131—133°), identical with the product, m.p. 78—81°, obtained by dehydrogenating staphisine (**I**) (cf. A., 1942, II, 40). The main hydrocarbon, $C_{19}H_{20}$, from (**I**) is probably a methylretene with the second Me in position 2, 3, or 4. It is oxidised by CrO_3–AcOH at 100° (bath) to a quinone, m.p. 213—216°, further oxidised by $KMnO_4$ to (probably) a *hydroxyisopropylphthalic acid* (**II**), $C_{11}H_{12}O_5$, melts with effervescence at ~170°, resolidifies and melts at ~290—294°. (**II**) is not found in the $KMnO_4$ oxidation products of retenequinone, but in addition to hydroxy*iso*propyldiphenyltricarboxylic acid, m.p. ~186—192° (cf. Ruzicka *et al.*, A., 1931, 360), a new acid, $C_{10}H_6O_7$, probably a dicarboxyphenylglyoxylic acid, is isolated as the *Me*$_3$ ester (**III**), m.p. 149—151°.

XIV. The hydrocarbon, $C_{17}H_{18}$ (probably 1 : 6- or 6 : 1-methylethylphenanthrene), obtained by dehydrogenating atisine is oxidised by CrO_3–AcOH at 100° (bath) for 7 hr. and then at 0° for 24 hr. to a *quinone*, $C_{17}H_{14}O_2$, m.p. 149—151°, further oxidised ($KMnO_4$) to a *diphenyltetracarboxylic acid* (**IV**), m.p. 340—345°, with decomp. and sublimation and probable anhydride formation (*Me*$_2$ ester, m.p. 149—150°, hydrolysed by aq. NaOH–MeOH to a *Me* ester, m.p. 338—341°). Attempts to oxidise (**IV**) by fuming HNO_3 and a little $Mn(NO_3)_2$ at 100° (bath) afford only a *monoanhydride*, m.p. 338—340°, of (**IV**). After separation of (**IV**) in the above oxidation, the mother-liquors are esterified (CH_2N_2 in $COMe_2$) to yield the Me$_3$ ester, m.p. 93—98°, of (?) hemimellitic acid, and (after hydrolysis with aq. HCl at 110° in a sealed tube) (?) trimellitic acid, m.p. 220—227°. In addition to the above Et_2O-extracted acid oxidation products, an acid is obtained which yields a Me$_3$ ester, m.p. 148—149°, identical with (**III**). A. T. P.

Veratrine alkaloids. XXI. Conversion of rubijervine into *allo*-rubijervine. The sterol ring systems of rubijervine. W. A. Jacobs and L. C. Craig (*J. Biol. Chem.*, 1944, **152**, 641—643; cf. A., 1943, II, 246, 313).—Rubijervine (**I**), like solanidine, possesses the regular steroidal skeleton, with a six-membered ring B. (**I**) and Cu (in CO_2) at 150—200° for 15 min., then 200—290° for 15 min., at 1 atm., then 290°/0·1 mm. for 1 hr., yield *rubijervone* (**II**), m.p. 202—204° (slight previous sintering). Its *oxime* melts largely at 160°, resolidifies, and remelts at ~247—254° (depends on rate of heating). (**II**) and Al(OPr^B)$_3$ yield a product, $C_{27}H_{43}O_2N$, softens to a melt at 218—220°, isomeric with (**I**) and probably containing *allo*- + *epi*-

allo-rubijervine. This transformation is analogous to that of cholestenone and *allo*cholesterol; the original suggestion that $C_{(5)}$ in (I) carries an ang. Me is improbable. A. T. P.

Comparative study of *Boerhaavia diffusa*, Linn., and the white- and red-flowered varieties of *Trianthema portulacastrum*, Linn. R. N. Chopra, N. R. Chatterjee, and S. Ghosh (*Indian J. Med. Res.*, 1940, **28**, 475—480).—Extraction with EtOH of the three plants used as the drug "Punarnava," yielded KNO_3: *B. diffusa* 0·36%, *T. portulacastrum* (white) 1·7%, *T. portulacastrum* (red) 2·6%. Extraction of the NH_3-alkaline mother-liquors with $CHCl_3$ and pptn. with Et_2O yielded a crude alkaloid, punarnavine, m.p. ~175° (decomp.) (*picrate*, m.p. 118—120°; *chloroplatinate*, m.p. 121—122° (cf. A., 1936, 652). The yield (on dry wt.) of drug was 0·04, 0·02, and 0·05%, respectively. S. E. M.

Alkaloids in *Adenocarpus intermedius*. I. Rivas (*Anal. Fís. Quím.*, 1942, **38**, 197—198).—The leaves contain 1·28% of alkaloids (cf. Santos Ruiz and Albiñana, B., 1942, III, 275). F. R. G.

Alkaloids of the seeds of *Delphinium consolida*, L.—See A., 1944, III, 516.

VIII.—ORGANO-METALLIC COMPOUNDS.

Organo-metallic compounds. I. Silver methyl, ethyl, and *n*-propyl. G. Semerano and L. Riccoboni (*Ber.*, 1941, **74**, [*B*], 1089—1099).—$PbMe_4$ and $AgNO_3$ in EtOH at −80° give AgMe or, if an excess of $AgNO_3$ is used, the compound, $AgMe,AgNO_3$. This is stable at −50°, but decomposes rapidly at −35°, giving Ag and C_2H_6 with traces of CO_2 and CO. $PbEt_4$ and $AgNO_3$ at −80° give a ppt. (AgEt) which decomposes when warmed to give Ag, C_2H_6 53, C_2H_4 10, and C_4H_8 37% with traces of CO. $Pb{Pr^n}_4$ and $AgNO_3$ in EtOH at −80° give a similar ppt. ($AgPr^n$), which is less stable, decomp. at ~−60° to give Ag (1 atom) and <1 mol. of (C_3H_8 + C_3H_6) with, presumably, C_6H_{14}. Clearly the decomp. is $AgR \rightarrow Ag + R\cdot$, followed by dimerisation and disproportionation of R· (except for R = Me) and small amounts of reduction by R·. The initial reaction is: $Ag^+ + PbR_4 \rightarrow AgR + PbR_3^+$. AgAlk are not explosive but are thermally less stable than AgAryl. R. S. C.

Mode of reaction of halogenated hydrocarbons with lithium phenyl [(VI)] and mechanism of the Wurtz–Fittig synthesis. G. Wittig and H. Witt (*Ber.*, 1941, **74**, [*B*], 1474—1491).—Exchange of Li and halogen occurs when sufficient electro-negative groups are present, the Li going to the more anionic component. In the series, *o*-OMe·C_6H_4·Hal, reactivity is I > Br > Cl, F. With aryl-alkyl chlorides exchange occurs only if $CHCl_3$ is absent (cf. below). CH_2PhBr (2 mols.) and LiPh (1 mol.) give $(CH_2Ph)_2$ and PhBr in almost 100% yield; $CHPh_2Br$ (1) and LiPh (1 mol.) give PhBr and $(CHPh_2)_2$ (90%); CPh_2Br_2 (2 mols.) and LiPh (1 mol.) give, by way of Li·CPh_2Br, PhBr (~100%), C_2Ph_4, and tar. CH_2Br_2 (1) and LiPh (1 mol.) give ~25% of PhBr and, by way of CH_2PhBr + LiBr, mainly CH_2PhBr and $(CH_2Ph)_2$. Interaction of $CHBr_3$ or CBr_4 is still more complex, but gives ~40% of PhBr. CCl_4 similarly gives PhCl and an inseparable mixture. $CPhCl_3$ gives very rapidly PhCl (30%) and a tar. CPh_2Cl_2 (1) and LiPh (1 mol.) give more slowly PhCl (30%) and C_2Ph_4. CPh_2Cl (1) and LiPh (1 mol.) give $(CPh_3\cdot O)_2$ and CPh_4, but no PhCl. $CHPh_2Cl$ (1) and LiPh (1 mol.) give $(CHPh_2)_2$ (30%). Exchange of H for Li depends on the "acidifying" nature of the substituent (F > Cl > Br > I > OMe > Ph). Thus, CH_2PhCl (1) and LiPh (1 mol.) give $CHPh_2\cdot CH_2Ph$ (I) (52%) by way of Li·$CHPhCl$ and Li·$CHPh_2$; CH_2Ph_2 does not react with LiPh and is thus not an intermediate. *Benzyl fluoride* (prep. from $CHPhN_2$ by HF–Et_2O; 18% yield), b.p. 60—61°/55 mm., gives CH_2Ph_2 (24%), (I) (27%), and other products. $CHPhCl_2$ reacts rapidly to give a tar, not containing PhCl. Loss of HCl can also occur with unreactive halides, but the factors governing this reaction are not yet clear. CHPh:CHBr (1 mol.) and LiPh (2 mols.) give CHPh:CHLi, whence $COPh_2$ gives $OH\cdot CPh_2\cdot C\cdot CPh$ (II) (54%). CHPh:CHCl (1 mol.) with LiPh (2 mols.) gives, after hydrolysis, CPh·CH (70%) and PhCl, but with I mol. of LiPh and then $COPh_2$ gives (II) (32%) and $CPh_3\cdot OH$ (also formed by initial reaction at −30°). Bu^nI and LiPh at 100° (no reaction at room temp.) give $CMe_2{:}CH_2$ (60%). Bu^nCl also does not react at room temp. *cyclo*-Hexyl iodide at 100° gives 71% of *cyclo*hexene, but the fluoride is unaffected by LiPh. The "side-reactions" thus revealed for organo-metallic compounds suffice to allow full interpretation of the Wurtz–Fittig reaction on the basis of formation of NaR. R. S. C.

IX.—PROTEINS.

Formula for agar. V. C. Barry and T. Dillon (*Chem. and Ind.*, 1944, 167).—*Gelidium latifolium* is bleached in sunlight, boiled for several hr. with distilled H_2O (which does not become acid), and filtered. The filtrate sets to a stiff jelly which after being twice frozen and thawed gives an agar (I) with 2·59% of ash and S 0·364%. This does not yield glyoxal when left in contact with HIO_4 for 6 months. Since the *l*-galactose (II) units are linked in the chain through $C_{(4)}$ each of them would, if they were ordinary (I) units, contain a pair of adjacent CH·OH groups. The absence of such groups, proved by the stability of (I) to HIO_4, shows that the 3 : 6-anhydro-*l*-galactose isolated from (I) as its 2 : 6-Me_2 derivative (Jones *et al.*, A., 1942, II, 219) is not an artefact produced during methylation but a constituent of (I). Secondly, >1% of S (if any) can be present in the mol. of (I) as SO_4 groups attached to $C_{(6)}$ of the (II) units. Thirdly, the mol. of (I) cannot contain as much as one non-reducing end group for every 140 galactose units. This result agrees with the absence of detectable quantities of tetramethylgalactose in the product of hydrolysis of methylated (I) (Percival *et al.*, A., 1943, II, 56). H. W.

Complex affinity of heavy metals for proteins. II. Effect of acidity on flocculation of proteins by silver salts. Binding of silver by proteins and organic nitrogen compounds. W. Haarmann and E. Frühauf-Heilmann (*Biochem. Z.*, 1941, **309**, 13—31).—Proteins differ very greatly in the extent to which they are pptd. from unbuffered solutions by $AgNO_3$, gelatin not being pptd. even by high concns. There are also great variations in the optimum pH for pptn., the val. for serum-albumin, ψ-globulin, and hæmoglobin being 7·5 and that for ovalbumin, casein, and euglobulin 5·0. With gelatin, capability for flocculation increases as pH increases. The Ag-binding power of proteins and NH_2-acids (*e.g.*, alanine, glycine, tyrosine) increases with increase in alkalinity, 2—3 times as much being bound at pH 10 as at pH 7. K_2CrO_4 serves as indicator of the extent of formation of complex Ag–protein and $-NH_2$-acid compounds. The extent varies greatly with the N compound used. W. McC.

Ferritin and *apo*ferritin in the ultracentrifuge. A. Rothen (*J. Biol. Chem.*, **152**, 1944, 679—693).—Results from the ultracentrifuging of ferritin (I) solution showed that ferritin is a mixture of a colourless, homogeneous protein and a coloured, heterogeneous material. The former proved to be identical with *apo*ferritin (II), a protein already isolated from (I) by removing the Fe. The latter appeared to be a complex of $Fe(OH)_3$ micelles of various sizes combined with (II). The mol. wt. of (II) is 465,000, and the mol. has an asymmetry of the same order as ovalbumin. J. F. M.

Effect of acylating agents on thiol groups of crystalline ovalbumin. H. Fraenkel-Conrat (*J. Biol. Chem.*, 1944, **152**, 385—389).—At pH 5—6, PhNCO and C_3O_2 reacted more readily with the ·SH groups of cryst. ovalbumin than with either the phenolic or NH_2-groups. Keten reacted with a greater proportion of NH_2-groups than of ·SH groups of the native protein. Esters formed by any of the reagents were hydrolysed by alkali at room temp.; reversible acylation of ·SH groups was demonstrated also with cysteine and glutathione. G. D.

Partial hydrolysis products from the action of proteolytic enzymes on casein.—See A., 1944, III, 500.

X.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Lignin. XLVI. Action of glycol chlorohydrin on pine lignin. K. Freudenberg and L. Acker (*Ber.*, 1941, **74**, [*B*], 1400—1406).—Heating pine-wood with $Cl\cdot[CH_2]_2\cdot OH$ (I) gives an alkali-sol. lignin (II) with 3% of $OH\cdot[CH_2]_2\cdot O\cdot[CH_2]_2\cdot Cl$, *methylene di-β-chloroethyl ether*, b.p. 93—94°/11 mm. [also obtained by heating (I), $(CH_2O)_x$, HCl, and $CaCl_2$], and traces of PhOH and a β-chloroethyl-hexoside [? -glucoside] (*tetra-acetate*, m.p. 105°, $[\alpha]_D^0$ +46° in $CHCl_3$). (II) contains ~14% of hexosan and 6% of Cl, due to retained (I); when allowance is made for this, the analysis shows loss of C, undoubtedly connected with a much decreased yield (0·5—1%) of CH_2O obtained by the action of conc. acid. This loss of CH_2O is held to come from CH_2O_2 groups, although various model substances are not thus affected by heating in (I). *Methylene dibenzyl ether*, b.p. 179—182°/11 mm., is described. R. S. C.

Isolation of gliotoxin and fumigacin from culture filtrates of *Aspergillus fumigatus*. A. E. O. Menzel, O. Wintersteiner, and J. C. Hoogerheide (*J. Biol. Chem.*, 1944, **152**, 419—429).—The fumigacin of Waksman *et al.* (cf. A., 1943, III, 770) is a mixture of fumigacin and gliotoxin; the latter contributes most of the antibiotic activity. Fumigacin is identical with helvolic acid, isolated from *A. fumigatus* culture medium by Chain *et al.* (cf. A., 1943, III, 917). The prep. of *fumigacin Me ester*, $C_{30}H_{40-42}O_7$, m.p. 260—261° (*oxime*, m.p. 204—206°; *semicarbazone*, m.p. 225—228°), is described. R. L. E.

Toxic principle of poison ivy and other related plants. D. Wasserman and C. R. Dawson (*J. Chem. Educ.*, 1943, **20**, 448–453).—A review. L. S. T.

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A II—Organic Chemistry.

AUGUST, 1944.

I.—ALIPHATIC.

Cinchona alkaloids. VI. Configuration of (−)-γ-methyl-δ-ethylhexane. V. Prelog and E. Zalan (*Helv. Chim. Acta*, 1944, **27**, 545—547).—The configuration (*A*) is established for (−)-γ-methyl-δ-ethylhexane (**I**) by its prep. from (−)-CHMeEt·CO_2Me. (−)-CHMeEt·CO_2H, b.p. 71—72°/12 mm., $[\alpha]_D$ −17·35°±0·05°, is converted by CH_2N_2 into the *Me* ester, b.p. 108—112°/730 mm., $[\alpha]_D^{15}$ −19·42°±0·05°, which with MgEtBr in Et_2O affords (+)-*γ-methyl-δ-ethylhexan-δ-ol*, b.p. 63—65°/11 mm., $[\alpha]_D^{16}$ +17·1°±0·05°. This is dehydrated by anhyd. $H_2C_2O_4$ to the corresponding hexene, which is hydrogenated (PtO_2 in AcOH) to (**I**), b.p. 155—162° (bath), $[\alpha]_D^{16}$ −3·18°±0·05°. H. W.

Et·CH·Et
H·C·Me
Et (*A*.)

Polymerisation of *iso*butene on hydrated silicate catalysts.—See A., 1944, I, 180.

Diolefines from allylic chlorides. II. A. L. Henne and H. H. Chanan (*J. Amer. Chem. Soc.*, 1944, **66**, 392—394; cf. A., 1942, II, 126).—Treating 1 : 1 mixtures of (*a*) CH_2:CH·CH_2Cl, CH_2:CMe·CH_2Cl, or butadiene hydrochloride and (*b*) piperylene hydrochloride or isoprene hydrochloride with Mg in Et_2O gives diolefines in which the *as.* product predominates. Compositions are determined by fractionation. Structures are proved by reduction and ozonolysis. The following are new: *δ-methyl-*$\Delta^{\alpha\epsilon}$*-heptadiene*, b.p. 110·3°; *δε-dimethyl-*$\Delta^{\beta\zeta}$*-octadiene*, m.p. −64·8°, b.p. 153·3°; *βδ-*, b.p. 132·1°, and *γδ-dimethyl-*$\Delta^{\alpha\epsilon}$*-n-heptadiene*, b.p. 129·8°; *γγ-dimethyl-*$\Delta^{\alpha\epsilon}$*-n-hexadiene*, b.p. 101·6°; *β-methyl-*$\Delta^{\beta\zeta}$*-n-heptadiene*, b.p. 119·1°; *γγζ-trimethyl-*$\Delta^{\alpha\epsilon}$*-n-heptadiene*, b.p. 149·7°; *βη-dimethyl-*$\Delta^{\beta\zeta}$*-n-octadiene*, m.p. −74·4°, b.p. 168·6°; *βδδ-trimethyl-*$\Delta^{\alpha\epsilon}$*-n-hexadiene*, b.p. 126·3°; *βζ-dimethyl-*$\Delta^{\alpha\epsilon}$*-n-heptadiene*, m.p. −102·7°, b.p. 141·9°; *βε-dimethyl-*$\Delta^{\beta\zeta}$*-n-heptadiene*, b.p. 134·6°; *δε-dimethyl-n-octane*, b.p. 162·4°; *γδ-dimethyl-*, b.p. 140·1°, and *βεε-trimethyl-*n*-heptane*, b.p. 152·8°; γ-keto-α-methyl-*n*-valeric acid semicarbazone, m.p. 178° (lit. 191°, 182°). B.p. are corr. R. S. C.

Conjugated diolefines by double bond displacement. II. A. L. Henne and H. H. Chanan (*J. Amer. Chem. Soc.*, 1944, **66**, 395—396; cf. A., 1942, II, 294).—Conversion of unconjugated into conjugated dienes in presence of Al_2O_3 is greatly improved by including 5 mol.-% of Cr_2O_3 in the catalyst (prep.: Grosse *et al.*, B., 1940, II, 260). The optimum temp. is 250°. The catalyst is gradually impaired by deposition of C but is regenerated by heating at 450°, first in air and then in H_2, but repeated treatment impairs the efficiency. $(CH_2$:CH·$CH_2)_2$ gives (CHMe:CH)$_2$ (76·7%). $(CH_2$:CMe·$CH_2)_2$ gives $(CMe_2$:CH)$_2$ (85·5%). CH_2:CH·CHMe·CH_2·CH:CHMe gives CHMe:CH·CH:CMeEt (73·1%). CH_2:CH·CH_2·CHMe·CH:CHMe gives CHMe:CH·CMe:CHEt (37·1%), b.p. 135·9°. CH_2:CH·[CHMe]$_2$·CH:CHMe gives CHMe:CH·CMe:CMeEt (22·6%), b.p. 156·5°. CH_2:CH·$[CH_2]_2$·CH:CMe_2 gives CHEt:CH·CH:CMe_2 (54·4%), m.p. −96·4°, b.p. 135·8°. CH_2:CH·CHMe·CH_2·CH:CMe_2 gives CMeEt:CH·CH:CMe_2 (48·9%), m.p. −63·1°, b.p. 156·9°. CH_2:CMe·CH_2·CHMe·CH:CHMe, CHMe:CH·[CHMe]$_2$·CH:CHMe, CH_2:CH·CMe_2·CH_2·CH:CMe_2, CMe_2:CH·$[CH_2]_2$·CH:CMe_2, and CH_2:CMe·$[CH_2]_2$·CH:CMe_2 are not thus rearranged. R. S. C.

Kinetics and mechanism of thermal polymerisation of acetylene and its reaction with nitric oxide. Mercury-photosensitised polymerisation of acetylene.—See A., 1944, I, 179, 180.

Dehydrochlorination of γ-chloro-Δ$^{\beta}$-propen-α-ol. Preparation of propargyl alcohol. L. F. Hatch and A. C. Moore (*J. Amer. Chem. Soc.*, 1944, **66**, 285—287).—The *α-* and *β-forms* of CH_2Cl·CH:CHCl in boiling 10% Na_2CO_3 give the *α-* (**I**), b.p. 146·3°/746 mm., and *β-forms* (**II**), b.p. 153·6°/756 mm., respectively, of *γ-chloro-*Δ$^{\beta}$*-propen-α-ol*. Up to 69·3% of CH:C·CH_2·OH is obtained from (**I**) by 10% NaOH, but (**II**) is unaffected except by >10% alkali, which causes resinification. R. S. C.

Optically active phytol. II. P. Karrer, H. Simon, and E. Z. Binden (*Helv. Chim. Acta*, 1944, **27**, 313—316; cf. A., 1944, II, 31).—The conversion of phytols (**I**) into phytadienes is accompanied by marked increase in optical activity and the products derived from (**I**) of differing dextrorotatory power or apparent optical inactivity have approx. the same rotation. Possibly (**I**) in spite of repeated fractionation retains a lævorotatory impurity which more or less compensates the dextrorotation of (**I**) or, more probably, pure natural (**I**) has an immeasurably small optical activity and the dextrorotation of many distilled specimens is due to a difficultly removable, dextrorotatory impurity (unidentified). At any rate it is established that natural (**I**) is not a racemate but an actual or latent optically active compound. Synthetic *l*-phytol (**II**) yields a *l*-phytadiene which has only slightly greater optical activity than the initial material and is much less active than the *d*-compound from natural (**I**). (**II**) and (**I**) are not therefore optical antipodes; (**I**) is probably racemic with respect to Distinction is drawn between: natural *d*-phytol (sterically homogeneous with respect to both asymmetric C atoms and probably having immeasurably small [α]) and *d*-phytadiene; synthetic *l*-phytol, sterically homogeneous with respect to $C_{(\delta)}$ and racemic at $C_{(\eta)}$ and synthetic *l*-phytadiene; synthetic *dl*-phytol, racemic in respect of both asymmetric C atoms, and optically inactive and synthetic *dl*-phytadiene. H. W.

Lead tetra-acetate oxidations in the sugar group. V. Rates of oxidation of open-chain polyalcohols in dry acetic acid. R. C. Hockett, (Miss) M. T. Dienes, H. G. Fletcher, jun., and H. E. Ramsden. **VI. Structures of di- and tri-benzoates of *D*-sorbitol and *D*-mannitol.** R. C. Hockett and H. G. Fletcher, jun. (*J. Amer. Chem. Soc.*, 1944, **66**, 467—468, 469—472; cf. A., 1944, II, 7).—V. Under standard conditions, the rate of oxidation of polyhydric alcohols, rapid at first and then slower, is independent of configuration but dependent on the no. of CH·OH in unbroken series. An empirical rule enables the no. of *vic.* CH·OH to be determined; reaction is not stoicheiometric as HCO_2H formed reduces more $Pb(OAc)_4$. The diacetamides of *D*-threose, -erythrose, -arabinose, and -lyxose behave similarly.

VI. Oxidation of *D*-sorbitol *αζ*-dibenzoate by $Pb(OAc)_4$ closely resembles that of erythritol and gives no CH_2O, which proves its structure. The structure of the *αβζ*-tribenzoate is similarly confirmed by consumption of 2 $Pb(OAc)_4$ without formation of HCO_2H. *D*-Sorbitol and BzCl in C_5H_5N at 20° give an *αβ*-dibenzoate and a small amount of *αβζ-tribenzoate* (**I**), m.p. 147·7—148·3° (corr.), $[\alpha]_D^{\cdot 8}$ −11·1° in $CHCl_3$. The structure of (**I**) is proved by consumption of 2 $Pb(OAc)_4$ and formation of *L*-OBz·CH_2·CH(OBz)·CHO and no CH_2O. R. S. C.

Structure of styracitol. R. C. Hockett and (Miss) M. Conley (*J. Amer. Chem. Soc.*, 1944, **66**, 464—466).—The structure of styracitol (**I**) as *αε*-anhydro-*D*-mannitol (A., 1944, II, 7) is confirmed. Hydroxyglucal tetra-acetate (**II**) with H_2–PtO_2 in AcOH at 23 lb., falling to ~45 lb., and then NaOMe–MeOH at 70° gives (**I**) (57%), m.p. 154—155°, $[\alpha]_D^{20}$ −50·9° in H_2O. Hydrogenation of (**II**) in MeOH and then boiling gives mainly a syrup, $[\alpha]_D^{20}$ +37·1° in EtOH, with only a trace of (**I**). Treating (**I**) with $Pb(OAc)_4$–$CHCl_3$ and then Br–$SrCO_3$–H_2O gives Sr *D*-hydroxymethyldiglycollate (44%). The Me_4 ether, b.p. 88—93°/2 mm., $[\alpha]_D^{0}$ −35·0° (homogeneous), with conc. HNO_3 at 100° gives *l*-$(OMe·CH·CO_2H)_2$ (cf. Asahina *et al.*, A., 1931, 1033), isolated as Me_2 ester and diamide. (**I**) gives a *m-nitrobenzylidene* derivative, m.p. 175—175·5°. R. S. C.

Stereochemistry of methylbixin. L. Zechmeister and R. B. Escue (*J. Amer. Chem. Soc.*, 1944, **66**, 322—330).—The methylbixins (photomicrographs) corresponding sterically to naturally occurring and *β*-bixin are termed "natural" (**I**), m.p. 161—161·5° (corr.), and "all-*trans*"-methylbixin (**II**), m.p. 198° (corr.), respectively. Isomerisation, followed by chromatography, yields also neomethylbixin *A*, m.p. 190—192° (corr.) (photomicrograph), *B*, and *C*, m.p. 150—151° (corr.) (photomicrograph). Light is needed for development of a *cis*-peak. Chromatograms and adsorption data are recorded for products obtained from each isomeride (except *B*) by melting, keeping, refluxing, or irradiating in light petroleum, or treating with I. (**II**) is very stable to light, and (**I**) nearly as stable, but *A* and *C* are more photosensitive. The changes, (**I**) *C* and (**II**) ⇌ *A*, are readily achieved, but the interconversion, (**I**) ⇌ (**II**), is very slow. The following configurations are probable: *A* 5-*cis*, (**I**) 2-*cis*, *C* 2 : 5-di-*cis*, and *B* x-*cis*. R. S. C.

Use of trimethyl phosphate as a methylating agent. A. D. F. Toy (*J. Amer. Chem. Soc.*, 1944, **66**, 499).—52·7—69·5% yields of ROMe are obtained by heating Me_3PO_4 with AlkOH at or just below the b.p., provided that this is ⩽160°. $(CH_2·OH)_2$ gives 37·2% of the Me_2 ether. An excess of Me_3PO_4 increases the yield. Some olefine

and mixed alkyl H phosphates are formed. *Me β-ethyl*-n-*hexyl*, b.p. 159—160°, and *β-heptyl ether*, b.p. 139—140°, are described. R. S. C.

Preparation of calcium and sodium formate.—See A., 1944, I, 182.

Alkyl exchange of carboxylic esters.—See A., 1944, II, 220.

Unsaturated synthetic glycerides. B. F. Daubert and H. E. Longenecker (*Oil and Soap*, 1944, **21**, 42—46).—Previous literature and recent work by the authors and collaborators (cf. A., 1944, II, 120) on the synthesis, by modern methods, and properties of mixed unsaturated–saturated glycerides of known configuration are reviewed, and graphs are given showing the m.p. and n_D of various series, viz., (*a*) unsymmetrical and (*b*) symmetrical mono-oleyl-disaturated (C_{16-18}) triglycerides; (*c*) unsymmetrical dioleyl-monosaturated triglycerides, (*d*) unsaturated–saturated symmetrical mixed diglycerides. In each series the m.p. of the corresponding products obtained by hydrogenation of the unsaturated glycerides are shown for comparison. All synthetic unsaturated glycerides show anomalous results in cryoscopic determinations (in C_6H_6) of mol. wt., the apparent mol. wt. decreasing with increasing concn., so that extrapolation to zero concn. is necessary in order to obtain true mol. wts. E. L.

Unsaturated synthetic glycerides. IV. Symmetrical mono-oleo-disaturated triglycerides. F. L. Jackson, B. F. Daubert, C. G. King, and H. E. Longenecker. **V. Unsymmetrical monoelaidyl-disaturated and monosaturated-dielaidyl triglycerides.** B. F. Daubert (*J. Amer. Chem. Soc.*, 1944, **66**, 289—290, 290—292; cf. A., 1944, II, 120).—IV. OH·CH_2·CH(OH)·CH_2·O·CPh_3 with RCOCl (R = saturated alkyl) in $CHCl_3$–C_5H_5N at 0° and then HCl–light petroleum at 0° gives the αγ-diesters, which with oleyl chloride in $CHCl_3$–quinoline at 100° give *glyceryl αγ-diacylate β-oleate*, in which the acyl is *n*-decoate, m.p. 5—6°, *n*-dodecoate, m.p. 14·5—15°, *n*-tetradecoate, m.p. 26—27°, palmitate, m.p. 35·5—36°, and stearate, m.p. 42·5—43°. Structures are confirmed by hydrogenation to fully saturated glycerides.

V. α-Monoelaidin, *forms*, m.p. 58·5°, 44·0°, and 17·6° (cf. Bomer *et al.*, A., 1937, II, 439), is obtained from *iso*propylideneglycerol by (*a*) *elaidyl chloride* (I) [prep. by ($COCl)_2$ at 70—80°], b.p. 168—170°/1 mm., in $CHCl_3$–quinoline and then HCl–Et_2O or (*b*) HCl–elaidic acid and then Et_2O–conc. aq. HCl. With saturated acyl chlorides in $CHCl_3$–quinoline it gives *glyceryl βγ-diacylate α-elaidate*, in which the acyl is *n*-tetradecoate, m.p. 39·5°, *n*-dodecoate, m.p. 27·0°, *n*-decoate, m.p. 15·0°, and *n*-octoate, m.p. 3·0°. α-Monomyristin and (I) in $CHCl_3$–quinoline give *glyceryl α-acylate βγ-dielaidate*, in which the acyl is *n*-tetradecoate, m.p. 40·0°, *n*-dodecoate, m.p. 35·5°, and *n*-decoate, m.p. 25·0°. Structures are proved by hydrogenation. *Glyceryl βγ-di*-n-*octoate α-stearate*, m.p. 31·5°, is prepared also solely from saturated acids. R. S. C.

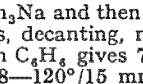
Synthesis of cetyl esters.—See A., 1944, II, 228.

Preparation of unsaturated fatty acid chlorides. T. R. Wood, F. L. Jackson, A. R. Baldwin, and H. E. Longenecker (*J. Amer. Chem. Soc.*, 1944, **66**, 287—289).—Oleic, elaidic, linoleic, and linolenic acids are converted by boiling ($COCl)_2$ into their *acid chlorides*, which are shown by their absorption spectra to contain $\geq$1% of conjugated material. Use of $SOCl_2$ is unsatisfactory. R. S. C.

Autoxidation reactions in polyisoprenes and allied compounds. VIII. Photo-oxidation of methyl elaidate. D. A. Sutton (*J.C.S.*, 1944, 242—243).—In ultra-violet light Me elaidate at 35° absorbs O_2 (0·2 mol.) to form a hydroperoxide, which on hydrogenation and hydrolysis followed by acetylation and fractional crystallisation gives a monohydroxystearic acid, m.p. 79°, and a OH-acid, m.p. 30—50°. D. G.

Condensations. XXII. Alkylation of *iso*propylmalonic ester using sodium triphenylmethide. J. C. Shivers, B. E. Hudson, jun., and C. R. Hauser (*J. Amer. Chem. Soc.*, 1944, **66**, 309; cf. A., 1944, II, 120).—Adding CPh_3Na and then EtI to $CHPr^{\beta}(CO_2Et)_2$ in Et_2O–N_2, keeping for 7 days, decanting, removing the Et_2O, and boiling the residue with EtI in C_6H_6 gives 73% of $CEtPr^{\beta}(CO_2Et)_2$, b.p. 234—236°/760 mm., 118—120°/15 mm., converted by KOH–EtOH and then decarboxylation into $CHEtPr^{\beta}\cdot CO_2H$ (48%), b.p. 104—105°/15 mm. (*anilide*, m.p. 118—119°). Use of $Pr^{\beta}I$ in C_6H_6–N_2 gives *Et*$_2$ *di*isopropylmalonate (23%), b.p. 122—124°/15 mm., converted by boiling KOH–EtOH in 18—24 hr. into the *Et H* ester, m.p. 71—72°, which is slowly decarboxylated by heat to give *Et β-methyl*-α-iso*propyl*-n-*butyrate*, b.p. 71—72°/15 mm. R. S. C.

Colour reactions of ascorbic acid.—See A., 1944, III, 488.

Ketones, ketonic acids, and enol-lactones. III. Enol-lactone fission. New preparation of esters of β-ketonic and ββ′-diketonic acids which are also αδ-diketones. P. Ruggli and A. Maeder (*Helv. Chim. Acta*, 1944, **27**, 436—443; cf. A., 1943, II, 351).—Et_2 butanolidenemalonate,  , (I), is best obtained (63% yield) by addition of (CH_2·$CO)_2O$ to $CHNa(CO_2Et)_2$ in boiling Et_2O. It is converted by CN·CHNa·CO_2Et in boiling Et_2O into *Et*$_3$ *βε-diketo-α-cyanohexane-αζζ-tricarboxylate*, an oil [*Cu* derivative, decomp. (indef.) ~180°], converted by $NHPh\cdot NH_2$ in cold AcOH into *Et* 1-*phenyl*-3-*γ-keto*-δ-*cyano*-δ-*carbethoxy*-n-*butylpyrazol*-5-*one*-4-*carboxylate*, m.p. 106—107° (green *Cu* compound), and in hot solution into α-4-*carbethoxy*-1-*phenyl*-3-*pyrazol*-5-*onyl*-β-4-*cyano*-1-*phenyl*-3-*pyrazol*-5-*onylethane*, m.p. 167—168°. CHAcNa·CO_2Et and (CH_2·$CO)_2O$ in C_6H_6 at room temp. and then at the b.p. afford *Et*$_2$ *βδηι-tetraketodecane-γθ-dicarboxylate* (Et_2 succinyldiacetoacetate) (II), m.p. 48° (*Cu* derivative, decomp. 235°), with some Et H β-keto-α-acetyladipate, m.p. 81—82°. (II) and $NHPh\cdot NH_2$ in hot 50% AcOH afford α-*di*-αβ-4-*carbethoxy*-1-*phenyl*-5-*methyl*-3-*pyrazolylethane* (III), m.p. 156—157°, which does not give a colour with $FeCl_3$. When kept overnight in Et_2O (I) and CHAcNa·CO_2Et give mainly Et_3 β-hydroxy-ε-keto-α-acetyl-Δ$^{\alpha}$-hexene-αζζ-tricarboxylate with some (II). The latter can be accumulated by the more rapid pptn. of its Cu compound, but separation or identification is best effected through (III) and α-4-*carbethoxy*-1-*phenyl*-3-*pyrazol*-5-*onyl*-β-4-*carbethoxy*-1-*phenyl*-2-*methyl*-3-*pyrazolylethane*, m.p. 114—115°. H. W.

Preparation of calcium *D*-altronate. P. P. Regna and B. P. Caldwell (*J. Amer. Chem. Soc.*, 1944, **66**, 244—246).—Enzymic hydrolysis of citrus pectin yields *D*-galacturonic acid, isolated as *Na Ca* salt, $(C_6H_9O_7)_3NaCa$, $+6H_2O$, $[\alpha]_D^0$ +33·0° in H_2O, which in aq. $Ca(OH)_2$–$CaCl_2$ gives completely (owing to insolubility of the product) basic Ca and thence normal *Ca δ-keto*-L-*galactonate*, $+5H_2O$, $[\alpha]_D^{20}$ −14·0° in H_2O, which with H_2–Raney Ni in H_2O at 80°/2300 lb. yields approx. equal amounts of Ca *L*-galactonate, $+5H_2O$, and *D*-altronate, $+3·5H_2O$, $[\alpha]_D^{20}$ +11·8° → 24·8—25·0° in ~90 min. in N-HCl, best separated by way of the derived Cd salts. R. S. C.

Synthesis of uronic acids. II. 2 : 3 : 4-Trimethyl derivatives of mannuronic, glucuronic, and galacturonic acids. F. Smith, M. Stacey, and P. I. Wilson (*J.C.S.*, 1944, 131—134).—α-Methylmannopyranoside in C_5H_5N with CPh_3Br gives 6-triphenylmethyl-α-methylmannoside, which with Me_2SO_4–NaOH in $COMe_2$ affords 6-*triphenylmethyl*-2 : 3 : 4-*trimethyl*-α-*methylmannoside*, m.p. 149°, $[\alpha]_D^{20}$ +27° in $CHCl_3$, from which the CPh_3 is removed (HCl) to yield 2 : 3 : 4-trimethyl-α-methylmannoside. Oxidation ($KMnO_4$) of this compound gives 2 : 3 : 4-trimethyl-α-methylmannuronoside. Similar oxidation of 2 : 3 : 4-trimethyl-β-methylglucoside and α-methylgalactoside affords respectively 2 : 3 : 4-trimethyl-β-methyl-α-glucuronoside and α-methyl-α-galacturonoside. *αβγ-Trimethyl-mannonolactone*, m.p. 74°, $[\alpha]_D^{20}$ +131° → +80° (equil.) in H_2O, and *-mannonamide*, m.p. 142°, $[\alpha]_D^{20}$ +5° in H_2O, are described. F. R. S.

Lactones of mannosaccharic acid. I. αδ-Dimethyl-Δ$^{\gamma}$-mannosaccharo-βε-lactone methyl ester. W. N. Haworth, (Miss) D. Heslop, (Miss) E. Salt, and F. Smith (*J.C.S.*, 1944, 217—224).—Mannosaccharodilactone (I) (prep. given) shows reducing properties after treatment with alkaline reagents, correlated with an absorption band at λ 2630 A. in alkaline solution, moving to 2290 A. on acidifying. Methylation of (I) gives similar isomerisation. With MeI and Ag_2O (I) gives Me$_6$ dimethyl*meso*tartrate (II), a trimethylmannosaccharolactone Me ester, and αδ-*dimethyl*-Δ$^{\gamma}$-*mannosaccharo-βε-lactone Me ester* (III), b.p. 152—158° (bath)/0·04 mm., $[\alpha]_D^{18}$ −25° in H_2O, absorption band at λ 2290 A. in H_2O. (III) is also obtained from (I) with CH_2N_2, or CH_2N_2 followed by MeI and Ag_2O, together with a little 6-carbomethoxy-3-methoxy-α-pyrone, m.p. 212°. The structure of (III) is confirmed by ozonisation, giving as final product mainly Me β-hydroxy-α-methoxyerythrosuccinate (IV), b.p. 105—110° (bath)/0·01 mm., $[\alpha]_D$ −43° in MeOH. On methylation (MeI and Ag_2O) (IV) gives (II), which with NH_3 in MeOH gives dimethoxyerythrosuccindiamide. With NH_3 in MeOH (IV) yields the *amide* of *β-hydroxy-α-methoxy*-l-*erythrosuccinic acid* (V), m.p. 153°, not optically active in H_2O. (IV) with NH_2Me in MeOH gives the *bismethylamide* of (V), m.p. 136°, $[\alpha]_D^{18}$ +10·7° in H_2O, identical with that prepared from *d*-araboascorbic acid (cf. A., 1944, II, 213). (III) on hydrogenation yields αδ-*dimethyl-γ-deoxymannosaccharo-βε-lactone Me ester*, b.p. 160° (bath)/0·03 mm., $[\alpha]_D^0$ −4° in H_2O, which affords αδ-*dimethyl-γ-deoxymannosaccharodiamide* (VI), m.p. 187°, $[\alpha]_D^{19}$ −74° in H_2O (negative Weerman test). The spatial arrangement in (VI) of the OMe and H on C_3 is not yet determined. Absorption curves for (III) and a comparable *l*-ascorbic acid derivative are given. The *diamide* of αββδ- (or αγδ-)trimethylmannosaccharic acid, m.p. 258° (decomp.), $[\alpha]_D^{20}$ −41° in H_2O, and the *half-amide NH*$_4$ *salt* of (V), m.p. 181° (decomp.), are described. D. G.

Preparation of α-ketopolyhydroxy-acids. P. P. Regna and B. P. Caldwell (*J. Amer. Chem. Soc.*, 1944, **66**, 243—244).—Dissolving *D*-glucono-γ-lactone and a little H_3PO_4 in boiling MeOH, adding $NaClO_3$ and V_2O_5, shaking at 20°, and then keeping at 3° gives Me α-keto-*D*-gluconate, m.p. 175—176°, $[\alpha]_D^{20}$ −76·8° in H_2O, hydrolysed by 2N-H_2SO_4 at 30° to the acid, which is isolated as *Ca* salt, $+3H_2O$, $[\alpha]_D^{20}$ −70·8° in H_2O. Shaking K *D*-galactonate, $KClO_3$, V_2O_5, and H_3PO_4 in H_2O and isolation by way of the *K* salt, $[\alpha]_D^{20}$ −6·7° in H_2O, gives α-*keto*-D-*galactonic acid*, m.p. 170—171°, $[\alpha]_D^{20}$ −6·0° in H_2O (Me ester, m.p. 138—139°, $[\alpha]_D^0$ −11·3° in H_2O). α-*D*-Glucohepto-γ-lactone, neutralised with aq. Na_2CO_3, gives similarly *Na* α-*keto*-D-*glucoheptonate*, $+H_2O$, $[\alpha]_D^0$ +45·5° in H_2O. Mixed α- and β-*D*-galactoheptonic acids give similarly *K* α-*keto*-D-*galactoheptonate*, $[\alpha]_D$ +67·5° in H_2O. R. S. C.

Condensations. XXIII. Acetylation of unsymmetrical aliphatic ketones with acetic anhydride in presence of boron trifluoride. C. R. Hauser and J. T. Adams (*J. Amer. Chem. Soc.*, 1944, **66**, 345—349; cf. A., 1944, II, 211).—Isomeric ketones are usually obtained at 0° from COMeAlk (1 mol.) by Ac_2O (2 mols.) saturated with BF_3. Thus, COMeEt gives only (100%) $CHMeAc_2$; $COMePr^{\alpha}$, n-C_5H_{11}·COMe, and n-C_6H_{13}·COMe give 90% of $CHEtAc_2$, $CHBu^{\alpha}Ac_2$, and n-C_5H_{11}·$CHAc_2$, respectively, with 10% of COAlk·CH_2Ac. $COMeBu^{\beta}$ gives 45% of *γ-acetyl-δ-methyl-*n*-pentan-β-one*, b.p. 183—185°/750 mm. (gives no enol test or Cu salt), and 59% of CH_2Ac·$COBu^{\beta}$; $COMePr^{\beta}$ gives 68% of *γγ-dimethyl-*n*-pentane-βδ-dione*, b.p. 172—174° (gives no enol or Cu salt), and 32% of CH_2Ac·$COPr^{\beta}$; 2-methyl-*cyclo*hexanone gives 50% each of 6- (purple $FeCl_3$ colour and oily Cu salt) and 2-*acetyl*-2-*methyl*cyclo*hexanone*, b.p. 220—222° (no enol colour or Cu salt). The mixed products are analysed by their ability or inability to dissolve in NaOH or give Cu salts. R. S. C.

***n*-Propyldi-*n*-butylamine.** T. D. Perrine (*J. Amer. Chem. Soc.*, 1944, **66**, 312).—$NHBu^{\alpha}_2$ (2 mols.) and $Pr^{\alpha}I$ (1 mol.) at 120° or NBu^{α}_2·$[CH_2]_3$·MgCl and aq. HCl give $NPr^{\alpha}Bu^{\alpha}_2$, b.p. 193°/754 mm., 73—75°/8 mm. (*picrate*, m.p. 115·8—116·2°). R. S. C.

Anhydrous tetramethylammonium compounds.—See A., 1944, I, 182.

Bismethylamides of α-hydroxy-β-methoxy-*d*- and *l*-erythrosuccinic acid. (Miss) D. Heslop, (Miss) E. Salt, and F. Smith (*J.C.S.*, 1944, 225—229).—*d*-Araboascorbic acid with CH_2N_2 gives *αβ-dimethyl*-d-*araboascorbic acid* (**I**), which with $CClPh_3$ in C_5H_5N yields *ε-triphenylmethyl-αβ-dimethyl*-d-*araboascorbic acid* (**II**), m.p. 174°, $[\alpha]_D^{18}$ −41° in $CHCl_3$ (gives no reaction with NH_3 in MeOH). This with MeI and Ag_2O gives *ε-triphenylmethyl-αβδ-trimethyl*-d-*araboascorbic acid*, $[\alpha]_D^{8}$ −28° in $CHCl_3$, hydrolysed to *αβδ-trimethyl*-d-*araboascorbic acid* (**III**), b.p. 170° (bath)/0·02 mm., m.p. 74°, $[\alpha]^{22}$ +10° in H_2O, which gives *αβδε-tetramethyl*-d-*araboascorbic acid* (**IV**), b.p. 130° (bath)/0·02 mm., $[\alpha]_D^{20}$ +9·5° in H_2O. (**I**), (**III**), and (**IV**) all show an absorption band at λ 2350 A. (**III**) on ozonisation and hydrolysis yields $H_2C_2O_4$ and β-methyl-*d*-erythronic acid (**V**), isolated on distillation of the Me ester as the *γ-lactone* (**VI**), m.p. 113°, $[\alpha]_D^{1}$ −108° in H_2O (no change on keeping). With NH_3 and NH_2Me respectively in MeOH (**VI**) gives the *amide*, m.p. 105°, $[\alpha]_D^{18}$ +36° in H_2O, and the *methylamide*, m.p. 82°, $[\alpha]_D^{17}$ +57·5° in MeOH, of (**V**), and with NH_3–MeOH after methylation (MeI, Ag_2O) the *amide*, m.p. 72°, $[\alpha]_D^{21}$ +55·5° in H_2O, of *αβ*-dimethyl-*d*-erythronic acid. On oxidation (HNO_3), esterification, and treatment with NH_2Me–MeOH, (**VI**) yields the bismethylamide of α-hydroxy-β-methoxy-*d*-erythrosuccinic acid, m.p. 136°, $[\alpha]_D^{18}$ +11° in H_2O, identical with that prepared from *αδ*-dimethyl-Δ^{γ}-mannosaccharolactone Me ester.(cf. A., 1944, II, 212). (**I**) with *p*-NO_2·C_6H_4·COCl in C_5H_5N gives *δε-di-*p*-nitrobenzoyl-αβ-dimethyl*-d-*araboascorbic acid*, a glass, which on ozonisation yields *Me βγ-di-*p*-nitrobenzoyl*-d-*erythronate*, m.p. 133°, $[\alpha]^{17}$ +29° in $CHCl_3$ (loses acyl groups on attempted methylation). *meso*Tartaric acid on partial methylation (Me_2SO_4 and NaOH) affords *dl*-CO_2H·$CH(OH)$·$CH(OMe)$·CO_2H, which is purified by distillation, b.p. 100—105° (bath)/0·04 mm., and crystallisation of the amide, m.p. 191°, or by distillation of the Me ester, b.p. 96—98° (bath)/0·01 mm., and resolved by brucine, the less sol. salt, $[\alpha]_D^{18}$ −23° in H_2O, giving β-hydroxy-α-methoxy-*d*-erythrosuccinic (α-hydroxy-β-methoxy-*l*-erythrosuccinic) acid, isolated as the *bismethylamide*, m.p. 135°, $[\alpha]^{20}$ −10·5° in H_2O.

D. G.

Structure-chemical investigations. IX. Adipdithioamide. H. Erlenmeyer and G. Bischoff (*Helv. Chim. Acta*, 1944, **27**, 412—413).—Addition of CN·$[CH_2]_4$·CN to NaOEt in EtOH saturated with H_2S at −10° followed by heating at 70° affords *adipdithioamide*, m.p. 180°, which is converted by COMe·CH_2Cl into *αδ-di-*4*-methyl*-2*-thiazolylbutane dihydrochloride*, m.p. 251°. H. W.

Cyanoalkylpyruvic esters from aliphatic nitriles. G. S. Skinner, J. H. Taylor, and J. L. Ernst (*J. Amer. Chem. Soc.*, 1944, **66**, 496—497).—In presence of NaOEt, $Bu^{\alpha}CN$ and $Et_2C_2O_4$ give 13%, in presence of KOEt give 55%, and in presence of 1 : 9 KOEt–NaOEt give 31%, of *Et α-keto-β-cyano-*n*-hexoate* (**I**), b.p. 135—137°/15 mm. (cf. A., 1937, II, 134). In presence of KOEt, $Pr^{\alpha}CN$ or n-C_5H_{11}·CN with $Et_2C_2O_4$ gives *Et α-keto-β-cyano-*n*-valerate* (65%), b.p. 127—129°/15 mm., and -n-*heptoate* (58%), b.p. 148—150°/15 mm., respectively. In presence of 1 : 1 NaOEt–KOEt, EtCN and $Et_2C_2O_4$ give 79% of CN·CHMe·CO·CO_2Et. With Et_2SO_4–NaOEt–EtOH, (**I**) give *Et β-cyano-α-ethoxy-*Δ^{α}-n*-hexenoate*, b.p. 114°/1 mm.

R. S. C.

Unsaturated esters of glycollonitrile. D. T. Mowry (*J. Amer. Chem. Soc.*, 1944, **66**, 371—372).—40% of OH·CH_2·CN (**I**), b.p. 99—100°/17 mm., is obtained by adding COMeEt and then NaCN to aq. $NaHSO_3$ at 0°, treating the product with 37% CH_2O + a little NaCN at 30°, and finally distilling with *o*-$C_6H_4(CO)_2O$. Adding RCOCl to CH_2O and NaCN in H_2O at 10° gives *CN·CH₂ acrylate* (17%), b.p. 60°/4 mm., *β-methylacrylate* (58%), b.p. 90—91°/10 mm., *crotonate* (60%), b.p. 103—104°/17 mm., *β-chlorocrotonate* (53%), b.p. 116°/16 mm., *cinnamate* (**II**) (73%), m.p. 63°, b.p. 164—165°/4 mm., and *α-methylcinnamate* (63%), b.p. 162—163°/3 mm. Adding (**I**) to RCOCl and $NPhMe_2$ in Et_2O at 10° gives (**II**) (75%), *CN·CH₂ fumarate* (45%), m.p. 83°, and *mesaconate* (43%), b.p. 192—193°/3 mm. R. S. C.

II.—SUGARS AND GLUCOSIDES.

Lead tetra-acetate oxidations in the sugar group. VII. Oxidation rates of ethyl β-*D*-galactofuranoside, methyl α-*D*-mannofuranoside, and γζ-anhydro-*D*-sorbitol. R. C. Hockett, M. H. Nickerson, and W. H. Reeder, tert. (*J. Amer. Chem. Soc.*, 1944, **66**, 472—474; cf. A., 1944, II, 210).—The OH attached to the ring of methyl-α-*D*-mannofuranoside (**I**) are *cis* and, as expected, the rate of oxidation by $Pb(OAc)_4$ under standard conditions is very rapid until 1 mol. has been consumed and then much slower, only traces of CH_2O being produced. The OH attached to the ring of ethyl-β-*D*-galactofuranoside are *trans*, so that they are not attacked by $Pb(OAc)_4$ faster than are the exocyclic C·OH; thus the rate of oxidation shows no break until >2 mols. have been consumed and CH_2O is formed in quantity (? 1 mol.). γζ-Anhydro-*D*-sorbitol (prep. from methyl-6-deoxy-α-*D*-glucopyranoside 6-iodide triacetate by way of 3 : 6-anhydro-*D*-glucose), m.p. 108—109°, oxidises, as expected, at a rate very similar to that of (**I**). CH_2Ac_2 consumes 3 mols. of $Pb(OAc)_4$ in an unbroken reaction. R. S. C.

3 : 6-Anhydrogalactose. II. 2-Methyl- and 4-methyl-3 : 6-anhydro-α-methylgalactopyranoside. (Mrs.) P. A. Rao and F. Smith (*J.C.S.*, 1944, 229—232; cf. A., 1940, II, 244).—α-Methylgalactopyranoside or its 6-*p*-toluenesulphonate (**I**) with *p*-C_6H_4Me·SO_2Cl–C_5H_5N gives *α-methylgalactopyranoside* 2 : 6-*di*-p-*toluenesulphonate* (**II**), m.p. 148°, $[\alpha]_D^{18}$ +68° in C_5H_5N. This with aq. 3N-NaOH gives 3 : 6-anhydro-α-methylgalactopyranoside, m.p. 139°, but with N-NaOH in aq. EtOH yields 3 : 6-*anhydro-α-methylgalactopyranoside* 2-p-*toluenesulphonate*, m.p. 138°, $[\alpha]_D^{18}$ +56° in $CHCl_3$, which with MeI and Ag_2O gives the 4-*Me* compound, m.p. 126°, $[\alpha]_D^{23}$ +88° in $CHCl_3$, hydrolysed with NaOH in aq. EtOH at 60° to 4-*methyl*-3 : 6-*anhydro-α-methylgalactopyranoside*, b.p. 110° (bath)/0·03 mm., m.p. 55°, $[\alpha]_D^{19}$ +81° in MeOH, $[\alpha]_D^{16}$ +75° in H_2O, yielding 2 : 4-dimethyl-3 : 6-anhydro-α-methylgalactoside, b.p. 100° (bath)/0·02 mm., $[\alpha]_D^{18}$ +75° in H_2O, which isomerises to the β-form, m.p. 83°, on treating with dry HCl. (**II**) with $COMe_2$ and H_2SO_4 gives the 3 : 4-*CMe_2* derivative, m.p. 148°, $[\alpha]_D$ +115° in C_5H_5N, also obtained from (**I**). This on methylation (MeI and Ag_2O) yields 2-*methyl*-3 : 4-iso*propylidene-α-methylgalactopyranoside* p-*toluenesulphonate*, m.p. 88°, $[\alpha]^{23}$ +99° in C_5H_5N, which is hydrolysed (1% HCl in MeOH) to 2-*methyl-α-methylgalactopyranoside* 6-p-*toluenesulphonate*, $[\alpha]_D^{23}$ +27° in EtOH, giving with NaOH in aq. EtOH 2-*methyl*-3 : 6-*anhydro-α-methylgalactopyranoside*, m.p. 102°, $[\alpha]_D^{16}$ +88° in H_2O. D. G.

Action of diazomethane on acyclic sugar derivatives. VI. *D*-Sorbose. M. L. Wolfrom, S. M. Olin, and E. F. Evans (*J. Amer. Chem. Soc.*, 1944, **66**, 204—206; cf. A., 1944, II, 6).—*aldehydo-D*-Xylose tetra-acetate (prep. from the Et_2 mercaptal tetra-acetate improved; cf. A., 1932, 146), m.p. 90—91°, $[\alpha]_D^{22}$ −23·3° in $CHCl_3$, by oxidation (cf. Major *et al.*, A., 1937, II, 49) and then treatment with PCl_5 in Et_2O gives D-*xylonyl chloride tetra-acetate*, m.p. 72—73°, $[\alpha]_D^{25}$ −14° in $CHCl_3$, whence CH_2N_2 in Et_2O yields 1-*deoxy*-1-*diazo*-keto-D-*sorbose tetra-acetate* (92%), m.p. 124·5—125·5°, $[\alpha]_D^{25}$ +44·5° in $CHCl_3$. In boiling AcOH this gives keto-D-*sorbose penta-acetate* (73%), m.p. 97·5—98·5°, $[\alpha]_D^{25}$ −2·5° in $CHCl_3$ (*oxime*, m.p. 113—114°, $[\alpha]_D^{23}$ −42° in $CHCl_3$), which, when crystallised with its *L*-isomeride, gives the DL-*form*, m.p. 83—84°. 0·6N-$Ba(OH)_2$ hydrolyses (**I**) to *D*-sorbose (80%), m.p. 158—160°, $[\alpha]_D^{26}$ +40·5° in $CHCl_3$. 1 : 8-Bisdiazomucyldimethane tetra-acetate with 47% HI in $CHCl_3$ gives *mucyldimethane tetra-acetate* (78%), m.p. 204—206°.

R. S. C.

Preparation of ββ-trehalose octa-acetate. C. M. McCloskey, R. E. Pyle, and G. H. Coleman (*J. Amer. Chem. Soc.*, 1944, **66**, 349—350).—*α-D*-Glucosyl bromide 2 : 3 : 4 : 6-tetra-acetate (**I**) (modified prep.) and β-*D*-glucose 2 : 3 : 4 : 6-tetra-acetate [prep. from (**I**) by H_2O and Ag_2CO_3 in $COMe_2$ at 0° and then 50—60°] give, by Schlubach and Scheteling's method (A., 1933, 148), >4% of *ββ*-trehalose octa-acetate, m.p. 180·5—181·5° (corr.), $[\alpha]_D^{1}$ +18·4° in $CHCl_3$, 18·8% condensation being indicated by the reducing val. By use of Ag_2CO_3, I, and $CaSO_4$ in EtOH the yield is raised to 10·5%, the reducing val. indicating 30—40% condensation (cf. A., 1936, 827).

R. S. C.

III.—HOMOCYCLIC.

Action of sulphuric acid on 1-phenyl-2-alkyl*cyclo*propanes. D. Davidson and J. Feldman (*J. Amer. Chem. Soc.*, 1944, **66**, 488—489).—Decomp. of the appropriate pyrazoline by Pt–asbestos and KOH gives 1-phenyl-*cyclo*propane, b.p. 174°, -2-methyl- (**I**), b.p. 184—186°, -2-*ethyl*- (**II**), b.p. 203—205°, and -2-iso*propyl*-cyclo*propane* (**III**), b.p. 213—216°. In 90% H_2SO_4 at 35—40°, (**II**) gives 1 : 1 : 2-trimethylindane, b.p. 208° (identified by oxidation to *o*-CO_2H·C_6H_4·CMe_2·COMe), but (**I**) and (**II**) give polymers. In 85% H_3PO_4 isomerisation to olefines occurs (no details are given). The *cyclo*propanes obey the modern version of Markovnikov's rule.

R. S. C.

Factors determining the course and mechanism of Grignard reactions. XII. Effect of cobaltous chloride on the reaction of magnesium methyl bromide with alicyclic chlorides. M. S. Kharasch, F. Engelmann, and W. H. Urry (*J. Amer. Chem. Soc.*, 1944, **66**, 365—367; cf. A., 1943, II, 284).—With MgMeBr–Et_2O at the b.p. (28 hr.), *trans-* (I) or *cis*-methyl*cyclo*hexane (II) gives methyl*cyclo*hexane (III) 10% and -hexene (IV) 33—34%, and *iso*bornyl chloride (V) gives a mixture (VI) (90%) of camphene and bornylene, but only 5% interaction occurs with bornyl chloride (VII); in all cases pure CH_4 is evolved. In presence of 5 mol.-% of $CoCl_2$, reaction is 86—98% complete in 5 hr.; (I) and (II) give (III) 28—34%, (IV) 23—31%, and di-2-methyl*cyclo*hexyl 22—27%, and the gas contains CH_4 77—83, C_2H_6 9—15, and C_2H_4 8%; *cyclo*hexyl chloride gives *cyclo*hexane 27, *cyclo*hexene 29, and di*cyclo*hexyl 26% with a gas containing CH_4 85, C_2H_6 9, and C_2H_4 6%; (V) gives camphane 19, (VI) 44, and dibornyl 31% with CH_4 77, C_2H_6 15, and C_2H_4 8%; (VII) gives camphane 15, (VI) 20, and dibornyl 63% with CH_4 72, C_2H_6 19, and C_2H_4 9%. The reactions thus differ from those with aliphatic chlorides (*loc. cit.*). The $CoCl_2$ results are explained as a free radical chain reaction, the electronic strength of the radicals playing a major part in determining the nature of the products. R. S. C.

Condensation of *cyclo*hexanol with halogenobenzenes in presence of sulphuric acid. R. Pajeau (*Compt. rend.*, 1942, **215**, 578—580).—*cyclo*Hexanol and PhCl or PhBr in presence of H_2SO_4 at room temp. give ~30% of *p*-chloro- or -bromo-*cyclo*hexylbenzene, respectively. H_2SO_4 + 60% oleum is used to give the corresponding I-derivative, which is oxidised by CrO_3–AcOH to *p*-$C_6H_4I{\cdot}CO_2H$. Similarly prepared are 4-chloro-3-methyl-, b.p. 150°/4 mm., and 5-chloro-2-methyl-*cyclo*hexylbenzene, b.p. 149°/14 mm. Examination of Raman spectra indicates absence of isomerides. A. T. P.

" Cyclisation " of vitamin-*A* and allied compounds. E. G. E. Hawkins and R. F. Hunter (*Biochem. J.*, 1944, **38**, 34—37).—" Cyclised " vitamin-*A* (I), m.p. 77—78°, max. at 372 mμ. 3760) has been obtained (cf. Shantz *et al.*, A., 1943, II, 257). Failure to " cyclise " (by HCl–EtOH) *β-apo*-2-carotenal, axerophthylidene-acetone (II) [max. at 395 mμ. 1460) and with $SbCl_3$ a max. at 735 mμ.], the C_{20}-aldehyde (III) [max. at 395 and 730 mμ. ($SbCl_3$)] of Haworth *et al.* (A., 1939, II, 114), and the alcohol prepared by Pondorff reduction of (III), suggests that a terminal OH is necessary for the reaction. This is not the only necessary condition, since *β-apo*-2-carotenol does not cyclise. The absence of OH in (I) (cf. Heilbron *et al.*, A., 1932, 1174) is confirmed (Zerevitinov). Axerophthylidene*iso*propyl alcohol [max. at 351 mμ. and 713 mμ. ($SbCl_3$)] [from (II) and $Al(OPr^{\beta})_3$] and 0·04N-HCl–EtOH give a " cyclised " product which shows max. at 420, 395, and 372 mμ. The results are discussed in connexion with the structure of vitamin-A_2, which undergoes " cyclisation " to a substance having max. identical with those of (I), but distinguishable from (I) by the absorption band at 693 mμ. ($SbCl_3$) (cf. Embree *et al.*, A., 1940, III, 321; Shantz *et al.*, A., 1943, II, 261). " Cyclised " subvitamin-*A* (IV) is formed in the product of " cyclisation " of the unsaponifiable matter of acetylated shark-liver oil and of a similar liver oil which is oxidised in stages by aeration. In the latter case, (IV) is present when ⩾80% of the original -*A* alcohol is destroyed, suggesting that (IV) is a primary oxidation product of -*A*, probably formed by attack of the double linking of the β-ionone ring in -*A* by O_2. A. T. P.

***spiro*Pentane.** M. J. Murray and E. H. Stevenson (*J. Amer. Chem. Soc.*, 1944, **66**, 314).—$C(CH_2Br)_4$ and Na in molten NH_2Ac containing also NaI and Na_2CO_3 give ~40% of spiro*pentane*, C_5H_8, b.p. 38·3—38·5°; olefines which are also formed are removed by successive treatment with aq. NH_3, aq. $AgClO_3$, and Br. The Raman spectrum and chemical inertness indicate the structure $C\left(<\!\!\begin{matrix}CH_2\\CH\end{matrix}\!\!>\right)_2$. The yield is ~1—5% in aq. MeOH. R. S. C.

1 : 2 : 3 : 4-Dibenzphenanthrene and its derivatives. II. Synthetic attempts. F. Bergmann and H. E. Eschinazi (*J. Amer. Chem. Soc.*, 1944, **66**, 183—184; cf. A., 1943, II, 296).—Δ^1-*cyclo*Hexenyl-*cyclo*hexanone (I) and 1-$C_{10}H_7{\cdot}MgBr$ in C_6H_6 give 2-*hydroxy*-2-α-*naphthyl*-$\Delta^{1',2'}$- or -$\Delta^{1:1'}$-*decahydrodiphenyl* (42%), b.p. 225—230°/0·8 mm., cyclised, best by $AlCl_3$ in C_6H_6 at 0° and then room temp., to 9 : 9-*spirocyclo*hexyl-3 : 4-tetrahydrobenzfluorene and an isomeride, b.p. 210—230°/0·1 mm. (*picrate*, m.p. 160—161°), and 250—270°/0·1 mm. (*picrate*, m.p. 169—170°), which with Se at 320° give 9 : 9-spirocyclo*hexyl*-3 : 4-*benzfluorene* (II), b.p. 225—230°/0·05 mm. (*picrate*, m.p. 141—142°). With $K_2Cr_2O_7$–AcOH at the b.p., (II) gives the 1 : 2-*quinone* (? a *p*-quinonoid isomeride), m.p. 228°. The structure of (II) follows from its absorption spectrum (following abstract) and its resistance to further dehydrogenation by Se or Pd–asbestos at 350°. The oily products obtained by Rapson (A., 1941, II, 95) as by-products of triphenylene ring-closures are probably also spirans. Interaction of Mg 9-phenanthryl bromide with (I), followed by cyclisation as above and dehydrogenation by Se at 350°, gives 9 : 9-*spirocyclo*hexyl-1 : 2 : 3 : 4-dibenzfluorene, b.p. 230—260°/0·2 mm. (brown *picrate*, m.p. 157—159°), with a smaller amount of 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-tetrabenznaphthalene [1 : 2 : 7 : 8-dibenzchrysene], b.p. 290—320°/0·1 mm. [reddish-black picrate, m.p. 210—212° (lit. 200°)]. R. S. C.

Spectrographic characterisation of a hydrocarbon synthesised by Bergmann and Eschinazi. R. N. Jones (*J. Amer. Chem. Soc.*, 1944, **66**, 185—186).—The structure of 9 : 9-*spirocyclo*hexyl-3 : 4-benzfluorene (preceding abstract) follows from the resemblance of its absorption spectrum [max. at 3150 (4·45), 3250 (4·43), 3395 (4·55), 3845 (1·38), 4105 (1·61), and 4360 A. (1·69) in EtOH; figures in parentheses are log $E_{mol.}$] to that of 3 : 4-benzfluorene and the difference thereof from those of chrysene and 3 : 4-benzphenanthrene. The absorption of the 1 : 2-quinone [max. at 2470 (4·28), 2680 (4·32), 3330 (3·94), and 4600 A. (3·49)] renders its formula probable but not certain. R. S. C.

Labile union of oxygen to carbon. Influence of supplementary cyclisations. C. Dufraisse and M. T. Mellier (*Compt. rend.*, 1942, **215**, 576—578).—1 : 9-5 : 10-Di-*o*-phenylenanthracene and 5 : 6-11 : 12-di-*o*-phenylenenaphthacene are stable to light in CS_2. The unsymmetrical 5 : 6-diphenyl- and 6-chloro-5-phenyl-11 : 12-*o*-phenylenenaphthacene afford the normal photo-oxides (62 or 20% yield, respectively), which are decomposed at 150° and 90° to give 24% and 5% of O_2, respectively, and CO_2. A. T. P.

Reaction between benzylamine and alkali metals. W. Krabbe and G. Grünwald [with E. Polzin and W. Menzel] (*Ber.*, 1941, **74**, [*B*], 1343—1352).—Bright colours are developed by NaNH₂ with NH_2R (R = $OH{\cdot}CPh_2{\cdot}CH_2$, $OH{\cdot}CHPh{\cdot}CHPh$, $OH{\cdot}CPh_2{\cdot}CHPh$, CH_2Ph, $Ph{\cdot}[CH_2]_2$, Ph, *p*-tolyl, *p*-C_6H_4Cl, *o*- and *m*-$NO_2{\cdot}C_6H_4$), $NH(CH_2Ph)_2$, $NHPh_2$, $N(CH_2Ph)_3$, NPh_3, C_5H_5N, or piperidine. $NH_2{\cdot}CH_2Ph$ gives a very similar colour (absorption spectrum) with Li in Et_2O; the absorption and conductivity with different proportions of $NH_2{\cdot}CH_2Ph$ and Li are determined; the solution contains a ~1 : 1 mixture of $LiNH_2$ and $LiNH{\cdot}CH_2Ph$. LiPh (prep. from PhBr) with $NH_2{\cdot}CH_2Ph$ in Et_2O yields a *compound*, $LiBr,2NH_2{\cdot}CH_2Ph$, m.p. 106°. R. S. C.

Theoretical study of the interaction of dimethylaniline and nitric acid. H. H. Hodgson (*J. Soc. Dyers and Col.*, 1944, **60**, 151—153).—With HNO_3 at 0°, $NPhMe_2$ gives 2 : 4 : 6 : 1-$(NO_3)_3C_6H_2{\cdot}NMe{\cdot}NO_2$ (HNO_3, *d* 1·52), or 2 : 4 : 6 : 1-$(NO_2)_3C_6H_2{\cdot}NHMe$ (*d* 1·42), or 2 : 4 : 1-$(NO_2)_2C_6H_3{\cdot}NMe_2$ (I) (*d* 1·34 and 1·254), or 3 : 5 : 3′ : 5′-tetranitrotetramethylbenzidine (II) (40%) + (I) (60%) (*d* 1·12); no reaction occurs with HNO_3 of *d* 1·046 and 1·024. With rise in temp., Me is expelled with HNO_3 of *d* 1·34 and 1·254, but not with acid of *d* 1·12. $NaNO_2$ accelerates, and $CO(NH_2)_2$ delays or inhibits, the reactions. Reactions of (II) with HNO_3 (*d* 1·52 and 1·42) are analogous to similar reactions of $NPhMe_2$ and (I). All the reactions are interpreted on the basis of modern electronic theory. A. T. P.

Preparation of selenocarbamides from carbodi-imides. F. Zetzsche and H. Pinske (*Ber.*, 1941, 74, [*B*], 1022—1024).—Di*cyclo*hexylcarbodi-imide, m.p. (microscope) 29—30°, and H_2Se in Et_2O give s-di*cyclohexylselenocarbamide*, decomp. 194°. Similarly are prepared s-*di*-p-*tolyl*- (I), m.p. 174° (decomp.), s-*di*-p-*dimethylaminophenyl*- (II), m.p. 183—185° (decomp. from 150°), s-*di*-l-*menthyl*-, m.p. 177° (decomp.), [α] −91·8°, and N-p-*dimethylaminophenyl*-N′-l-*menthyl*-, m.p. 147° (decomp.), [α] −38·4°, -*selenocarbamide* and, from the carbodi-imide salts, the *monomethiodide*, m.p. 187—188° (decomp.), and *monomethosulphate*, sinters 165°, m.p. 167—170° (decomp.), of (II). Selenocarbamides are unstable in air or when treated with oxidising agents or heated at 120° in vac. Acidic decomp. of (I) in air or H_2 gives *p*-$C_6H_4Me{\cdot}NC$ and Se, probably by way of *p*-$C_6H_4Me{\cdot}NCSe$. PhNCS decomposes (I) with pptn. of Se. R. S. C.

Sulphanilamide.—See B., 1944, II, 149.

Derivatives of sulphanilamide.—See B., 1944, III, 118.

New class of medicinal; polymethine colouring matters. Buu-Hoï (*Compt. rend.*, 1942, **215**, 580—582).—*p*-$NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$ (I) and CNBr in aq. C_5H_5N give α-*p*-sulphamylanilino-ε-*p*-sulphamylanilo-$\Delta^{\alpha\gamma}$-pentadiene. Furfuraldehyde (II), (I), and NH_2Ph,HCl in EtOH afford the hydrochloride of α-anilino-ε-*p*-sulphamylanilo-*o*-hydroxy-$\Delta^{\alpha\gamma}$-pentadiene. Analogous hydrochlorides are obtained by replacing NH_2Ph with *m*- and *p*-$C_6H_4Cl{\cdot}NH_2$ and -$C_6H_4Br{\cdot}NH_2$, *o*-, *m*-, and *p*-$C_6H_4R{\cdot}NH_2$ (R = NO_2, OMe, and Me), 2 : 4 : 1-$NO_2{\cdot}C_6H_3Me{\cdot}NH_2$, α- and β-$C_{10}H_7{\cdot}NH_2$, 1 : 2-$NO_2{\cdot}C_{10}H_5{\cdot}NH_2$, *p*-$NH_2{\cdot}C_6H_4{\cdot}N{:}NPh$, and 5 : 2 : 1-$NH_2{\cdot}C_6H_3(OH){\cdot}CO_2H$. *m*- and *p*-$C_6H_4(NH_2)_2$ yield compounds, $[p\text{-}NH_2{\cdot}SO_2{\cdot}C_6H_4{\cdot}N{:}CH{\cdot}C(OH){:}CH{\cdot}CH{:}CH{\cdot}NH]_2C_6H_4,2HCl$, and benzidine gives a similar derivative. $(p\text{-}NH_2{\cdot}C_6H_4)_2SO_2$, NH_2Ph,HCl, and (II) give the dihydrochloride, $[NHPh{\cdot}CH{:}CH{\cdot}CH{:}C(OH){\cdot}CH{:}N{\cdot}C_6H_4]_2SO_2,2HCl$; β-$C_{10}H_7{\cdot}NH_2$ reacts similarly to NH_2Ph, and diamines give more complex derivatives. Analogous compounds are obtained from NH_2Ph or β-$C_{10}H_7{\cdot}NH_2$ and $(p\text{-}NH_2{\cdot}C_6H_4)_2SO$. A. T. P.

1 : 4-Diammo*cyclo*hexane.—See B., 1944, II, 155.

Mechanism of the diazo-coupling reaction. III. Unusual coupling phenomena and their interpretation. H. H. Hodgson and E. Marsden (*J. Soc. Dyers and Col.*, 1944, **60**, 120—124).—An extension of views on the mechanism of the coupling reaction (A., 1943, II, 8; 1944,

II, 75) to cover apparently anomalous examples, *e.g.*, the weak and limited coupling of *o*-OH·C_6H_4·CO_2H, 1 : 3-NO_2·$C_{10}H_6$·OH, and 1 : 5-$C_{10}H_6(OH)_2$, and the polycoupling of resorcinol. There are also discussed the coupling of arylamines, the diazoamino- → aminoazo-conversion, the failure of *o*- or *p*-C_6H_4Me·NMe_2 to couple, and the coupling of aminonaphtholsulphonic acids, all from the resonance viewpoint. There is also discussed the effect of C_5H_5N in promoting the activity of weakly-coupling diazo-compounds, the diazo-exchange reaction, and the coupling of phenol ethers.

K. H. S.

Pyrolysis of lactic acid derivatives. Production of phenyl and *o*-tolyl acrylate. E. M. Filachione, J. H. Lengel, and C. H. Fisher (*J. Amer. Chem. Soc.*, 1944, **66**, 494—496).—Heating 80% OH·CHMe·CO_2H with AcOH, C_6H_6, and a trace of conc. H_2SO_4 with removal of H_2O gives OAc·CHMe·CO_2H (77%), converted by $SOCl_2$ into OAc·CHMe·COCl (82%), which with ArOH at 100° gives *Ph* (**I**) (86—88%), b.p. 143°/12 mm., and *o-tolyl α-acetoxypropionate* (**II**), b.p. 112—113°/<1 mm. Pyrolysis of (**I**) at 440—600° gives up to 80% of CH_2:CH·CO_2Ph, b.p. 63—64°/1—2 mm., and of (**II**) at 500—591° gives up to 75% of CH_2:CH·CO_2·C_6H_4Me-*o*, b.p. 55—57°/0·5 mm., with larger yields of AcOH and, from (**I**), up to 20% of styrene and some CO_2 and CO. The acrylates are stable unless washed with alkali; polymerisation yields relatively hard resins. R. S. C.

Halogenophenols.—See B., 1944, II, 197.

Diphenyl series. IV. Iodination of the acetate, benzoate, and benzenesulphonate of 4-hydroxydiphenyl. H. R. Schmidt, (Miss) C. M. Savoy, and J. L. Abernethy (*J. Amer. Chem. Soc.*, 1944, **66**, 491—494; cf. A., 1944, II, 12).—*p*-C_6H_4Ph·OAc with I and conc. HNO_3 in hot CCl_4 (38·3% yield) or AcOH (13·8% yield), or with ICl in AcOH (10·5% yield), gives *p*-C_6H_4I·C_6H_4·OAc-*p*, m.p. 155—156°, hydrolysed by KOH–EtOH–H_2O to *p*-C_6H_4I·C_6H_4·OH-*p* (**I**) (also obtained from benzidine) and obtained therefrom by Ac_2O and a little syrupy H_3PO_4. *p*-C_6H_4Ph·OR (R = Bz or $PhSO_2$) with I–HNO_3–AcOH or ICl–AcOH similarly gives *p*-C_6H_4I·C_6H_4·OR-*p* [R = *Bz*, m.p. 207°; *p*-C_6H_4Me·SO_2, m.p. 93·5° (corr.)], hydrolysed to and obtained from (**I**). R. S. C.

Preparation of phenolic esters. E. Baumgarten, H. G. Walker, and C. R. Hauser (*J. Amer. Chem. Soc.*, 1944, **66**, 303—304).—RCOCl and ArOH in C_5H_5N give 4-*diphenylyl* (82%), m.p. 74·2—74·8°, and *Ph* isobutyrate (87%), b.p. 111—112·2°/25·5 mm., and 4-*diphenylyl Et carbonate* (60%), m.p. 73·9—75·0°. R. S. C.

Nitrogenous derivatives of *dl*-γδ-di-*p*-hydroxyphenylhexane. L. Spitzer (*Gazzetta*, 1942, **72**, 445—450).—*dl*-(*p*-OH·C_6H_4·$CHEt)_2$ (Dodds *et al.*, A., 1939, II, 312) in C_6H_6 with dil. HNO_3 gives *dl*-γδ-di-(3-nitro-4-hydroxyphenyl)hexane (**I**), m.p. 114—115°, with ~5% of, probably, the *meso*-isomeride, m.p. 226—228°, also obtained by nitrating *meso*-(*p*-OH·C_6H_4·$CHEt)_2$. With Me_2SO_4–MeOH–KOH, (**I**) gives the aci-*form* (**II**), m.p. 106·5°, yellow, of *dl*-γδ-di-(3-nitro-4-methoxyphenyl)hexane, of which the normal *form* (**III**), m.p. 107—109°, almost colourless, is obtained by nitrating *dl*-γδ-di-(3-nitro-4-methoxyphenyl)hexane. Hydrogenation (Pd–C) of (**II**) or (**III**) gives dl-γδ-*di*-(3-*amino*-4-*methoxyphenyl*)*hexane*, m.p. 113—115° [picrate, m.p. 130—131°; $(COEt)_2$ derivative, m.p. 106—108°], the *Ac*$_2$ derivative, m.p. 152—153°, of which is oxidised by $KMnO_4$–$MgSO_4$ to 3 : 4 : 1-NHAc·C_6H_3(OMe)·CO_2H. E. W. W.

Synthesis of substances with very high œstrogenic activity. C. Mentzer and G. Urbain (*Compt. rend.*, 1942, **215**, 554—556).—*p*-OMe·C_6H_4·CH_2·CN (**I**) and EtBr–$NaNH_2$ give α-p-*anisylbutyronitrile*, (?) m.p. 130° (corresponding *acid*, m.p. 68°, and *amide*, m.p. 101—102°). (**I**) and *m*-OMe·C_6H_4·$[CH_2]_2$·Br similarly afford α-p-*anisyl*-γ-m-*anisylbutyronitrile*, b.p. 205—210°/3 mm., hydrolysed to the corresponding acid, which is cyclised ($POCl_3$) to 1-keto-6-methoxy-2-*p*-anisyl-1 : 2 : 3 : 4-tetrahydronaphthalene, convertible by MgMeI, followed by demethylation, into 6-hydroxy-2-*p*-hydroxyphenyl-1-methyl-3 : 4-dihydronaphthalene (cf. Salzer, A., 1943, II, 8), which shows œstrogenic activity in doses of 0·3—0·5 μg. A. T. P.

Cleavage of phenol ethers by pyridine hydrochloride. V. Prey (*Ber.*, 1941, **74**, [*B*], 1219—1225).—C_5H_5N,HCl (**I**), m.p. 144°, boils undecomposed at 218° and, acting as a strong acid, is very effective for dealkylation of ArOAlk, even for PhOMe. Heating with 3 parts of (**I**) at ~200° for 5—6 hr. usually gives 70—100% yields. Unstable substituents, *e.g.*, in anethole or *iso*eugenol, reduce the yield to 15—20%. Ph_2O is unaffected. All OAlk of polyhydric phenol ethers are hydrolysed, but conditions can be found for partial dealkylation; *e.g.*, for *o*- or *m*-$C_6H_4(OMe)_2$ use of 1·3 mols. of (**I**) and 5—15% of AcOH at 180—190° gives 6—75% of OMe,-ether. R. S. C.

Dissociation of hexa-arylethanes. XV. Methoxyl substituents. C. S. Marvel, J. Whitson, and H. W. Johnston (*J. Amer. Chem. Soc.*, 1944, **66**, 415—417; cf. A., 1943, II, 27).—Dissociation into free radicals, indicated by magnetic susceptibility, of OMe-substituted hexa-arylethanes is is indicated by cryoscopy (cf. Gomberg *et al.*, A., 1923, i, 211; Lund, A., 1927, 661). This is because the ethanes are unstable, giving low "mol. wts." by disproportionation. The following are reported: *m*-OMe·C_6H_4·CO_2Et (prep. by distilling the acid with H_2SO_4–EtOH–C_6H_6), b.p. 130—135°/15 mm.; *p*-OMe·CPh_2·OH, m.p. 60° (lit. 58—61°, 84°, 82°); *diphenyl*-m-*anisyl*-, m.p. 89—90°, and *tri*-m-*anisyl-methyl chloride*, m.p. 123—124°; *o*-, *D* (=dissociation for 0·1M. solutions in C_6H_6) 3·8%, *m*-, *D* 2·1—3·1%, and *p*-$(OMe·C_6H_4·CPh_2)_2$, *D* 3·8—5·2%; [(*o*-$OMe·C_6H_4)_2$CPh]$_2$, *D* 6·8—8·0%; $C_2(C_6H_4$·OMe-*o*$)_6$, *D* 52% (0·05M. solution); $C_2(C_6H_4$·OMe-*m*$)_6$, *D* 10%. R. S. C.

***o*-Phenylenedioxyacetic acid and its ethyl ester.** W. G. Christiansen and M. A. Dolliver (*J. Amer. Chem. Soc.*, 1944, **66**, 312).—*o*-$C_6H_4(OH)_2$ (**I**), $CHCl_2$·CO_2Et, and NaOEt (2 mols.) in EtOH–N_2 give *Et* o-*phenylenedioxyacetate*, b.p. 115—117°/12·5 mm., and thence (N-NaOH) the derived *acid*, m.p. 107—108°. $CHCl_2$·CO_2H does not condense with (**I**). R. S. C.

Salts of phenolsulphonic acids.—See A., 1944, I, 182, 183.

Mechanism of the reaction of (−)-phenylalkylcarbinols with hydrogen bromide. C. L. Arcus (*J.C.S.*, 1944, 236—239).—The view of Levene *et al.* (A., 1939, II, 155) that the three mechanisms of substitution (S_Ni; S_N2; S_N1) do not suffice to explain the rotation–temp. curves for the reactions between HBr and CHPhR·OH (R = Me, Et, Pr^n) is modified. If the part played by each mechanism in the total reaction is represented by a distribution curve about a max. at a certain temp., it is found that the algebraic sum of the optical results of the three mechanisms reproduces the experimental curves. The "domain" of each mechanism, represented by the area between its distribution curve and the temp. axis, is calc. for the three reactions. A. T. P.

Reaction of citronellal with magnesium benzyl chloride. W. G. Young and S. Siegel (*J. Amer. Chem. Soc.*, 1944, **66**, 354—358).—Citronellal (**I**) and an excess of CH_2Ph·MgCl in Et_2O give 80% of α-benzylcitronellol (**II**), b.p. 153—156°/3 mm., but use of an excess of (**I**) leads to 70—80% of o-α-*hydroxy*-β*ζ*-*dimethyl*-Δ^ε- (or -Δ^ζ-)n-*heptenyl*-β′-*hydroxy*-γ′η′-*dimethyl*-Δ$^{ζ'}$- (or -Δ$^{η'}$-)*octenylbenzene* (**III**), b.p. 234—235°/3 mm. (cf. Rupe, A., 1914, i, 131; Gilman *et al.*, A., 1930, 1409). The structure of (**III**) is proved by its mol. wt. in camphor or C_6H_6, possession of 2 active H (MgMeI) (and no CO), 2 OH (quant. interaction with Ac_2O), 2 C:C (Br; H_2–Pd–$BaSO_4$), 2 citronellyl radicals [with CrO_3 gives 2·61—2·66 AcOH, whereas (**II**) gives 1·14—1·16 AcOH], oxidation by $KMnO_4$–C_5H_5N to *o*-$C_6H_4(CO_2H)_2$ (**IV**) (but no BzOH), dehydration by $KHSO_4$ at 160°/<1 atm. to 2 : 6-*di*-αε-*dimethyl*-Δ^δ- (or -Δ^ε-)n-*hexenyl*-3 : 4-*benz*-Δ^3-*dihydro*-1 : 2-*pyran*, b.p. 215—217°/3 mm. [which is probably the substance isolated by Rupe (*loc. cit.*)], and by the different course of the following reaction. The aldol (prep. by KOH in 95% EtOH), b.p. 170·5—173°/5 mm., of (**I**) with CH_2Ph·MgCl gives the "normal" addition product, oxidised to BzOH with only traces of (**IV**), and dehydrated to a partly cyclised *hydrocarbon*, $C_{27}H_{40}$, b.p. 204—206°/3 mm. R. S. C.

Vinyl polymers. XVIII. Optically active styrene derivative and its polymer. C. S. Marvel and C. C. Overberger (*J. Amer. Chem. Soc.*, 1944, **66**, 475—477; cf. A., 1944, II, 123).—*d-sec.*-BuOH, $[\alpha]_D$ with Na and then *p*-C_6H_4Br·CH_2Br in boiling C_6H_6 gives p-*bromobenzyl* d-sec.-*Bu ether* (**I**) (49·1%), b.p. 109—110°/8 mm., $[\alpha]_D^{23}$ +10·2° in 95% EtOH. *p*-C_6H_4Br·CH_2·OMe, CuCN, and some C_5H_5N at 215—225° give 68% of *p*-CN·C_6H_4·CH_2·OMe (**II**), b.p. 108—110°/9 mm. Similarly, but with addition of a little $CuSO_4$ and *p*-C_6H_4Me·CN, (**I**) gives impure p-*cyanobenzyl* d-sec.-*Bu ether* (**III**) (90%), b.p. 134—137°/9 mm., $[\alpha]_D^{23}$ +10·9° (the *dl*-sec.-Bu ether also could not be completely purified), hydrolysed by KOH in boiling 95% EtOH to (? dl-)p-sec.-*butoxymethylbenzoic acid*, m.p. 77—78°. With an excess of MgMeI in Et_2O, (**II**) or (**III**) gives *p*-methoxymethylacetophenone (52%), b.p. 104—105°/9 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 170—171°), or p-d-sec.-*butoxymethylacetophenone* (**IV**) (65%), b.p. 129—130°/10 mm., $[\alpha]_D^{20}$ +10·8° in 95% EtOH (2 : 4-*dinitrophenylhydrazone*, m.p. 158—159°), respectively. Slow distillation of (**IV**) with $Al(OPr^\beta)_3$–$Pr^\beta OH$ then yields α-p-d-sec.-*butoxymethylphenylethyl alcohol* (60%), b.p. 144—149°/9 mm., $[\alpha]_D^{23}$ +11·2° in 95% EtOH, converted by $KHSO_4$ and a trace of quinol at 200—220°/60—100 mm. (N_2) into p-*vinylbenzyl* d-sec.-*Bu ether* (**V**) (47%), b.p. 111—113°/8 mm., $[\alpha]_D^{25}$ +12·8° in dry dioxan. (**V**) and some Bz_2O_2 in dioxan at 55° give a solid *polymer*, OBz·$[(C_{13}H_{18}O)_8O_{11}]_n$; during 27 hr. changes from +0·917° to +0·722°; measurement (±0·01°) is sufficiently accurate to indicate a first-order reaction. R. S. C.

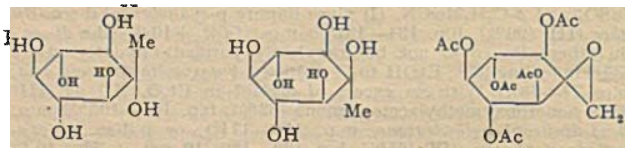
Electrolytic reduction of acetophenone in alkaline solution. S. Swann, jun., P. E. Ambrose, R. C. Dale, R. C. Rowe, H. M. Ward, H. D. Kerfman, and S. Axelrod (*Trans. Electrochem. Soc.*, 1944, **85**, *Preprint* 9, 93—99).—Of many metal cathodes examined in connexion with the alkaline electrolytic reduction of COPhMe in presence of EtOH and KOAc, Sn gave the highest yield of pinacol isomerides; 77% yield was obtained at 85° with c.d. 0·005 amp. per sq. cm. Yields at Cr, Mo, W, Bi, Pb, Zn, Cd, Hg, and Cu cathodes were good, at Fe moderate, and at Ni, Co, and Mg poor. C. R. H.

1-*n*-Alkyl*cyclo*pentanols and their derivatives. C. R. McLellan and W. R. Edwards, jun. (*J. Amer. Chem. Soc.*, 1944, **66**, 409—

412).—*cyclo*Pentanone and MgRBr give 1-methyl-, m.p. 36°, b.p. 81°/100 mm. (p-*nitro*-, m.p. 83°, and 3 : 5-*dinitro-benzoate*, m.p. 115·5°), 1-ethyl-, m.p. —10°, b.p. 74·5°/20 mm. (p-*nitro*-, m.p. 52·5°, and 3 : 5-*dinitro-benzoate*, m.p. 108·3°), 1-*n*-propyl-, m.p. —37·5°, b.p. 83°/20 mm. (p-*nitro*-, m.p. 59·5°, and 3 : 5-*dinitro-benzoate*, m.p. 82°), 1-*n*-butyl-, b.p. 99°/20 mm. (p-*nitro*-, m.p. 31°, and 3 : 5-*dinitro-benzoate*, m.p. 75·3°), 1-*n*-hexyl-, b.p. 124°/20 mm. (3 : 5-*dinitrobenzoate*, m.p. 86·5°), 1-*n*-heptyl-, b.p. 136·5°/20 mm. (p-*nitro*-, m.p. 26°, and 3 : 5-*dinitro-benzoate*, m.p. 76·8°), 1-n-*octyl*-, m.p. —17·5°, b.p. 135·5°/9 mm. (3 : 5-*dinitrobenzoate*, m.p. 77°), 1-n-*decyl*-, m.p. —18°, b.p. 133°/7 mm. (slight decomp.) (3 : 5-*dinitrobenzoate*. m.p. 78°), 1-n-*dodecyl*-, m.p. 2°, b.p. 142·5°/3 mm. (decomp.) (3 : 5-*dinitrobenzoate*, m.p. 81·3°), and 1-n-*tetradecyl*-cyclo*pentanol*, m.p. 16·2°, b.p. 164·5°/2 mm. (decomp.) (3 : 5-*dinitro-benzoate*, m.p. 81·5°). Condensation with PhOH (methods: Huston *et al.*, A., 1937, II, 494; Welsh *et al.*, A., 1938, II, 94) gives 1-p-*hydroxyphenyl*-1-*methyl*-, m.p. 95·5°, *-ethyl*-, m.p. 96·3°, b.p. 137°/2·5 mm. (2′ : 6′-Br_2-derivative, m.p. 97°), -n-*propyl*-, m.p. 67·5°, b.p. 135°/1 mm. (2′ : 6′-Br_2-derivative, m.p. 104·5°), -n-*butyl*-, m.p. 57·5°, b.p. 151°/2 mm. (2′ : 6′-Br_2-derivative, m.p. 69°), -n-*hexyl*-, m.p. 61·8°, b.p. 163°/2·1 mm., -n-*heptyl*-, m.p. 53·5°, b.p. 174°/2·5 mm., and -n-*octyl*-cyclo*pentane*, m.p. 42·8°. B.p. at various pressures (apparatus: C, 1944, Part 3), d_4^0, d_0^{25}, and parachors are given for the *cyclo*pentanols; plotting *d* against the no. of C shows an abrupt change at alkyl = C_7, and the same break is shown by *d* of the alkyl*cyclo*pentanes; this is due to the packing being governed for the lower alkyl derivatives by the size of the *cyclo*pentane ring but for the higher alkyl by the size of the alkyl. The phenols in which alkyl = Me—Bu are approx. equally bacteriostatic (*Staph. aureus*), but the higher alkyl derivatives are ineffective. R. S. C.

Stereochemistry of cryptoxanthin and zeaxanthin. L. Zechmeister and R. M. Lemmon (*J. Amer. Chem. Soc.*, 1944, **66**, 317—322).—Irradiation (sunlight) of dil. solutions (1—10 mg. per 100 ml.) of cryptoxanthin (I) or zeaxanthin (II) in light petroleum causes bleaching due to stereoisomerisation, structural conversion into other pigments, and cleavage to colourless or almost colourless substances; these changes occur in the order stated but overlap; they are faster for (II) than for (I). I in light petroleum (also melting or keeping or refluxing in solution in the dark) causes isomerisation, but light (even for a few sec.) is needed for development of a *cis*-peak. Adsorption orders and absorption max. are detailed. The following structures are probable: neocryptoxanthin B 6-*cis*, U 3- or 9-*cis*, and A 6 : *x*-di-*cis*-cryptoxanthin; neozeaxanthin A 6-*cis*, B 5-*cis*, and C (? 6 : *x*-)di-*cis*-zeaxanthin. R. S. C.

Cyclitol series. VII. Cyclitol (mytilitol) of mussels and related substances. T. Posternak (*Helv. Chim. Acta*, 1944, **27**, 457—468; cf. Jansen, A., 1931, 791; Ackermann, A., 1921, i, 764).—Mytilitol (I) is (*A*) and iso*mytilitol* (II) is (*B*). (I), m.p. 266—268° (slight decomp.) (hexa-acetate, two forms, m.p. 181° and ~170° and 181° after re-solidification), gives 1 mol. of AcOH when oxidised by CrO_3, showing it to be a *C*-methylinositol; under like conditions quercitol does not afford AcOH appreciably. (I) is obtained synthetically by the action of a large excess of MgMeI followed by $Ba(OH)_2$ on either form of the penta-acetate of scyllo*meso*inosose (III); it is accompanied by a small proportion of (II). Either penta-acetate and CH_2N_2 in well-cooled $CHCl_3$–Et_2O affords *penta-acetoxymethylene*cyclo*nexane oxide* (IV), m.p. 213°, hydrogenated



(*A.*) (*B.*) (IV.)

(PtO_2 in glacial AcOH) to iso*mytilitol penta-acetate*, m.p. 226—228°. This is resistant towards CrO_3–AcOH and Ac_2O–C_5H_5N at room temp. and is hydrolysed [$Ba(OH)_2$–MeOH] to (II), rhombs or occasionally long needles, m.p. 225—226° [*hexa-acetate* (boiling Ac_2O containing conc. H_2SO_4 or, preferably, $ZnCl_2$), m.p. 188—189°]. (III) and CH_2N_2 give *pentahydroxymethylene*cyclo*hexane oxide* (V), gradual decomp. >250° in a capillary, m.p. 244—247° (block), hydrogenated to (II). Boiling Ac_2O containing anhyd. $FeCl_3$ or $ZnCl_2$ converts (IV) or (V) into the *hepta-acetate*, m.p. 158—159°, of *hydroxymytilitol* (VI) (also +0·5H_2O), m.p. 247° after softening. With boiling Ac_2O–NaOAc or –KOAc, (IV) gives the *hexa-acetate* (VII), m.p. 185—186°, of *hydroxy*iso*mytilitol* (VIII), m.p. 223°, transformed by boiling Ac_2O–$ZnCl_2$ into the *hepta-acetate*, m.p. 191—192°. (IV) and HBr–AcOH at room temp. give *bromo*-iso*mytilitol penta-acetate*, m.p. 219—220°, which with Ac_2O–H_2SO_4 yields a peracetate, m.p. 191°, and with KOAc gives (VII). *Hydroxy*iso*mytilitol penta-acetate mono*-p-*toluenesulphonate*, m.p. 187—188° (decomp.; rapid heating) [from (IV) and anhyd. *p*-$C_6H_4Me{\cdot}SO_3H$ in $CHCl_3$], NaI, and $COMe_2$ at 110° afford *iodo*iso*mytilitol penta-acetate*, m.p. 227—231°. (I) is oxidised by HIO_4 less rapidly than (II), thus proving that all the successive OH groups in (I) are *trans*-to one another. Similar differences in the rate of oxidation are found for scyllitol and *meso*-inositol and for (VI) and (VIII), respectively. H. W.

Organic sulphur compounds. New sulphide and its derivatives. A. Cabra Fernández and M. Cabanzón Martínez (*Anal. Fís. Quím.*, 1942, **38**, 400—404).—CHPhPr^{n}Cl with K_2S–EtOH gives *di-α-phenyl-n-butyl sulphide*, b.p. 160—165°/40 mm. (*sulphoxide*, m.p. 50°; *sulphone*, m.p. 56—57°). F. R. G.

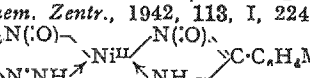
Coupling αβ-unsaturated compounds with diazonium salts. C. F. Koelsch and V. Boekelheide (*J. Amer. Chem. Soc.*, 1944, **66**, 412—415).—When ArN_2Cl reacts with CHR:CHR′ in presence of the aq. NaOAc and $CuCl_2$, the first reaction is reversible formation of Ar·N:N·OAc, followed by irreversible dissociation into Ar·, AcO·, and N_2. Then follow the reactions, (i) Ar· + CHR:CHR′ → CHArR·CHR′· (*A*), (ii) Cu^{++} + (*A*) → Cu^+ + CHArR·CHR′$^+$ (*B*), and (iii) Cu^+ + AcO· → Cu^{++} + OAc^-. The direction of addition of Ar· in (i) is governed by the natures of R and R′. The final reaction is (*B*) + Cl^- → CHArR·CHR′Cl (*C*) or (*B*) → H^+ + CArR:CHR′, according to the natures of R and R′. If R′ = CO_2H, (*C*) is formed; if R = CO_2H, (*B*) is decarboxylated. Since the rate of evolution of N_2 varies for different olefines, formation of a complex must precede formation of NAr:N·OAc. Yields are poor and much tar is formed. CHMe:CH·CO_2Et (I) and *p*-$C_6H_4Cl{\cdot}N_2Cl$ (II) etc. (in $COMe_2$ at 20°) give *Et α-chloro-β-*p*-chlorophenyl-*n*-butyrate* (34%), b.p. 125—140°/2—3 mm., converted by KOH–MeOH into *p*-$C_6H_4Cl{\cdot}CMe{:}CH{\cdot}CO_2H$ (II), m.p. 134° (turbid; clear at 138·5°) [also obtained from *p*-$C_6H_4Cl{\cdot}CMe(OH){\cdot}CH_2{\cdot}CO_2Et$, b.p. 160—162°/11 mm], partly converted by warm conc. H_2SO_4 into a stereoisomeride, m.p. 92—99° (lit. 94°). Non-formation of $CHMeCl{\cdot}CH(C_6H_4Cl\text{-}p){\cdot}CO_2Et$ in the condensation is proved by boiling the crude product in $NPhEt_2$, hydrolysing the resulting ester, hydrogenating (H_2–Raney Ni; NaOH; 40 lb.), and treating with PCl_5 and then with $AlCl_3$ in C_6H_6, which gives mainly (40%) 3-methylindanone. PhN:Cl and (I) etc. at 20—35° give $CHPhMe{\cdot}CHCl{\cdot}CO_2Et$ (7·5%), b.p. 100—104° (some decomp.)/4 mm., recognised by conversion into the known $CPhMe{:}CH{\cdot}CO_2H$. $CHMe{:}CH{\cdot}CO_2Me$ and 2 : 4 : 1-$C_6H_3Cl_2{\cdot}N_2Cl$ etc. in aq. $COMe_2$ at 5° give 2 : 4 : 1-$C_6H_3Cl_2{\cdot}CHMe{\cdot}CHCl{\cdot}CO_2Me$ (20%) (cf. A., 1939, II, 262), converted by KOH–MeOH into *β*-2 : 4-*dichlorophenylcrotonic acid*, m.p. 126—127°, which is hydrogenated (Raney Ni; aq. NaOH) to $CHPhMe{\cdot}CH_2{\cdot}CO_2H$. $CHMe{:}CH{\cdot}CO_2H$ and *p*-$NO_2{\cdot}C_6H_4{\cdot}N_2Cl$ etc. in aq. $COMe_2$ at 0° followed by MeOH–HCl give *Me α-chloro-β-*p*-nitrophenyl-*n*-butyrate*, b.p. 175—180° (some decomp.)/3 mm., whence *p*-$NO_2{\cdot}C_6H_4{\cdot}CMe{:}CH{\cdot}CO_2H$ is obtained. $CHPh{:}CH{\cdot}CO_2Me$ and (II) etc. in aq. $COMe_2$–C_5H_5N at 30° give $CHMeCl{\cdot}CH(C_6H_4Cl\text{-}p){\cdot}CO_2Me$ (cf. *loc. cit.*). $CHPh{:}CH{\cdot}CH{:}CH{\cdot}CO_2H$ and PhN_2Cl etc. in aq. $COMe_2$ at 10° give $(CHPh{:}CH)_2$ (28%). $CHPh{:}CH{\cdot}CH{:}CH{\cdot}CO_2Me$ with PhN_2Cl etc. at 15° gives $CHPh{:}CH{\cdot}CH{:}CPh{\cdot}CO_2Me$ (19%) and with (II) etc. gives, after hydrolysis, *δ-phenyl-α-*p*-chlorophenyl-*$\Delta^{\alpha\gamma}$*-pentadienoic acid*, m.p. 233—234°. Sorbic acid and PhN_2Cl give $CHMe{:}CH{\cdot}CH{:}CHPh$ (26%). R. S. C.

Reactions of *tert.*-butyl cinnamate and benzoate with magnesium phenyl bromide. F. Frostick, E. Baumgarten, and C. R. Hauser (*J. Amer. Chem. Soc.*, 1944, **66**, 305).—Adding $CHPh{:}CH{\cdot}CO_2Bu^\gamma$ (0·115) to MgPhBr (0·23 mol.) in Et_2O and then boiling gives only (44%) *Bu$^\gamma$ ββ-diphenylpropionate*, m.p. 55·5—55·6°, identified by hydrolysis. $Bu^\gamma OBz$ (0·3) and MgPhBr (0·5 mol.) in Et_2O at room temp. and then the b.p. give $CPh_3{\cdot}OH$ (41%) and BzOH (10%), but not $CMe_2{:}CH_2$ or $PhBu^\gamma$. R. S. C.

[Alkyl exchange of] carboxylic esters. II. F. Adickes and V. Krawczyk (*Ber.*, 1941, **74**, [*B*], 1389—1394).—Occurrence of the exchange, RCO_2Et + MeOH → RCO_2Me + EtOH, cannot be predicted from the nature of R. It occurs readily (70% in 8 hr. at the b.p. with 10 mols. of anhyd. MeOH) with Et 2-hydroxythionaphthen-1-carboxylate *S*-dioxide (I) (derived *Me* ester, m.p. 177—180°), fairly readily (~5—10%) with $CH(CO_2Et)_3$, $CN{\cdot}CHPh{\cdot}CO_2Et$, $(CO{\cdot}CO_2Et)_2$, or Et 1-bromo-2-keto-1 : 2-dihydrothionaphthen-1-carboxylate *S*-dioxide (? *Me hemiacetal*, m.p. 90°), slightly (~1—3%) with $CN{\cdot}CPh(CO_2Et)_2$ or the Me ether of (I), and not with $C(CO_2Et)_4$, Et_2 fumarate and *r*-tartrate, $(\cdot C{\cdot}CO_2Et)_2$, $CO_2Et{\cdot}CH_2{\cdot}NH_2{,}HCl$, $CN{\cdot}CH_2{\cdot}CO_2Et$, $OH{\cdot}CPh_2{\cdot}CO_2Et$, $CPh_2F{\cdot}CO_2Et$, $CN{\cdot}CPh_2{\cdot}CO_2Et$, $(OPh)_2C(CO_2Et)_2$, *p*-$C_6H_4Me{\cdot}SO_2{\cdot}CHPh{\cdot}CO_2Et$, Et nicotinate, and 2-hydroxy- or 2-methoxy-coumarone-1-carboxylate. R. S. C.

Hydrogenolysis of benzyl esters in contact with nickel catalysts. Y. R. Naves (*Helv. Chim. Acta*, 1944, **27**, 261—268).—Esters of $CH_2Ph{\cdot}OH$ suffer rapid hydrogenolysis in contact with Raney Ni at room temp. and < atm. pressure, whereas esters of alcohols and phenols apparently closely related to $CH_2Ph{\cdot}OH$ are changed slowly or not at all. A possible means is afforded of evaluating CH_2Ph esters in essential oils, natural perfumes, etc. $CHPh{:}CH{\cdot}CO_2CH_2Ph$ readily absorbs 2 H_2 at 30° with formation of PhMe and $Ph{\cdot}[CH_2]_2{\cdot}CO_2H$; after union with 1 H_2 the product contains PhMe, $Ph{\cdot}[CH_2]_2{\cdot}CO_2CH_2Ph$, and $Ph{\cdot}[CH_2]_2{\cdot}CO_2H$ but no $CHPh{:}CH{\cdot}CO_2H$. The product of the reaction at 135—140°/10 atm. is $(CH_2Ph{\cdot}CH{\cdot}CO_2H)_2$. Hydrogenolysis in contact with Raney Ni in presence of EtOH or EtOAc of CH_2Ph acetate, laurate, succinate, benzoate, and salicylate

is rapid and complete at a low temp. $CH_2Ac{\cdot}CO_2Et$ behaves individually on account of the simultaneous decomp. of $CH_2Ac{\cdot}CO_2H$. Dioxan inhibits and $NPhMe_2$ retards hydrogenolysis. There is little hydrogenolysis of anisyl, *p*-tolylcarbinyl, *p*-cuminyl, dl-*phenylmethyl-*, b.p. 72—73°/4 mm. [not identical with the product thus described by Kenyon *et al.* (A., 1933, 604)], or phenylethyl-carbinyl acetate, and practically no hydrogenolysis with *phenyldimethylcarbinyl acetate*, b.p. 81—82°/2·8 mm., $Ph{\cdot}[CH_2]_2$ acetate or phenylacetate, or $CH_2Ph{\cdot}CO_2{\cdot}C_6H_4Me$-*p*. Cinnamyl cinnamate, *trans-iso*eugenol acetate, and eugenol benzoate are hydrogenated without appreciable hydrogenolysis. H. W.

Complex of nickel with toluamidoxime. L. Malatesta and R. Pizzotti (*Gazzetta*, 1942, **72**, 564—567).—$Ni(OAc)_2$ and *p*-$C_6H_4Me{\cdot}C(NH_2){:}N{\cdot}OH$ in KOH–EtOH, followed by H_2O_2, give not a Ni^{IV} (Kuras, *Chem. Zentr.*, 1942, **113**, I, 2244), but a Ni^{II} *compound*, $C_6H_4Me{\cdot}C$  $C{\cdot}C_6H_4Me$, which is similar to that obtained by Malatesta (*Gazzetta*, 1940, **70**, 842) from $NH_2{\cdot}CPh{:}N{\cdot}OH$; with HCl it evolves N_2. E. W. W.

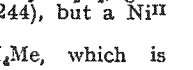
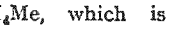
Action of formaldehyde on *m*-hydroxybenzoic acid. I. C. A. Buehler, T. A. Powers, and J. G. Michels (*J. Amer. Chem. Soc.*, 1944, **66**, 417—418).—*m*-$OH{\cdot}C_6H_4{\cdot}CO_2H$ (I) and 40% CH_2O in conc. HCl–H_2SO_4 at 30—40° give 3-*hydroxyphthalide* (CO = 1) (II), m.p. 254° [*Me* (III), m.p. 127°, and *Et ether*, m.p. 170°; *acetate*, m.p. 96—97°], and a substance, m.p. 175°. KOH–$KMnO_4$ at 60—75° converts (III) into 3 : 1 : 2-$OMe{\cdot}C_6H_3(CO_2H)_2$ [Me_2 ester, m.p. 73—74° (lit. 71°)]. Br and (I) in AcOH at 50° give 3 : 4 : 6 : 1-$OH{\cdot}C_6H_2Br_2{\cdot}CO_2H$, the Me ether, m.p. 205° (lit. 202—203°), of which with $CH_2(OMe)_2$–conc. HCl–H_2SO_4 at 50—55° gives 4 : 6-*dibromo-3-hydroxyphthalide*, m.p. 146°, reduced to (II) by H_2–Raney Ni at 150—200°/500 lb. R. S. C.

Derivatives of di-iodohydroxybenzoic acids.—See B., 1944, II, 156.

Reactions of *o*-substituents during stilbene syntheses. E. Macovski, J. Georgescu, and C. Bachmeyer (*Ber.*, 1941, **74**, [*B*], 1279—1284).—2 : 1 : 4-$CN{\cdot}C_6H_3Me{\cdot}NO_2$ with 30% H_2O_2 in boiling MeOH–H_2O–KOH gives 4-*nitro-o-toluamide* (Me = 1) (I), m.p. 175° (resistant to NaOMe–MeOH at room temp.), which with NaOMe–PhCHO–MeOH at room temp. gives 4-*nitrostilbene-2-carboxylamide* (II), m.p. 263° (partial decomp.), and with *o*-$NO_2{\cdot}C_6H_4{\cdot}CHO$ (III)–NaOMe–MeOH gives 4 : 2′-*dinitrostilbene-2-carboxylamide*, m.p. 228°. With (III) at 140—150°, (I) gives *o-nitrobenzylidene-NN′-bis-4′-nitro-o-toluamide*, m.p. 253°, but with RCHO–NaOMe–MeOH at room temp. gives 4-*nitro-*, m.p. 206° [with, in one experiment, (II)], and 4 : 2′-*dinitro-stilbene-2-carboxylic acid*, m.p. 210°. R. S. C.

Reaction of γ-anisyl-γ-butyrolactone with potassium cyanide. 6-Methoxy-1 : 2 : 3 : 4-tetrahydro-2-naphthoic acid. C. C. Price and W. Kaplan (*J. Amer. Chem. Soc.*, 1944, **66**, 477—478).—*p*-$OMe{\cdot}C_6H_4{\cdot}CO{\cdot}[CH_2]_2{\cdot}CO_2H$ (prep. modified to give a 95% yield), m.p. 144°, when esterified by boiling with EtOH in a Soxhlet extractor with removal of H_2O by CaC_2 in the thimble and then heated with $Al(OPr^\beta)_3$–$Pr^\beta OH$ with very slow removal of $COMe_2$, gives 79% of cryst. γ-*p*-anisyl-γ-*n*-butyrolactone. Interaction thereof with KCN at 210° (N_2) involves rearrangement, yielding *β-cyano-γ-p-anisyl-n-butyric acid* (I), m.p. 116·5° (corr.) (cf. Blaise, A., 1897, i, 323), the structure of which is proved as follows. With HF at 100° (not H_2SO_4 or, as chloride, $AlCl_3$) and then conc. H_2SO_4 at room temp. (1 week), (I) gives 4-*keto*-6-*methoxy*-1 : 2 : 3 : 4-*tetrahydro-2-naphthoamide*, m.p. 178° (corr.) [*oxime*, m.p. 217—219° (corr.)], reduced by 10% Pd–C–H_2 in EtOH at 41 lb. to 6-*methoxy*-1 : 2 : 3 : 4-*tetrahydro-2-naphthoamide* (II) (68%), m.p. 141° (corr.). Thence HCl–H_2O–AcOH at the b.p. yields the *acid* (III) (85%), m.p. 151° (corr.), not demethylated by KOH–EtOH or HBr–AcOH–H_2O. S at 210—245° converts (II) into a thioamide, which with KOH–EtOH gives 6 : 2-$OMe{\cdot}C_{10}H_5{\cdot}CO_2H$, m.p. 194—196° (lit. sinters 190°, m.p. 209°) [amide, m.p. 220—221° (lit. 219°)]. R. S. C.

Haloform reaction. R. T. Arnold, R. Buckles, and (Miss) J. Stoltenberg (*J. Amer. Chem. Soc.*, 1944, **66**, 209—210).—In aq. MeOH the haloform reaction applied to Ac compounds may lead directly to Me esters owing to the intermediate $CO{\cdot}CCl_3$ reacting faster with MeOH than with H_2O (cf. acid chlorides). 5-Methoxy-1 : 2 : 3 : 4-tetrahydronaphthalene, Ac_2O, and $AlCl_3$ in $PhNO_2$ at 0—5° give 5-acetyl-8-methoxy-1 : 2 : 3 : 4-tetrahydronaphthalene (I), b.p. 164—166°/8 mm. [*oxime*, m.p. 136—139° (decomp.)], which with $Ca(OCl)_2$, KOH, and K_2CO_3 in aq. MeOH gives *Me* 8-*methoxy*-1 . 2 : 3 : 4-*tetrahydronaphthalene-5-carboxylate* (II) (80%), m.p. 63—64°, and a small amount of the corresponding *acid* (III), m.p. 215·5—216° [with CH_2N_2 gives (II)]. With $Ca(OCl)_2$ and KOH (excess) in aq. dioxan, (I) gives 7-*chloro*-8-*methoxy*-1 : 2 : 3 : 4-*tetrahydronaphthalene-5-carboxylic acid*, m.p. 154—156°, which is obtained very rapidly by chlorination of (III) and is not obtained in the haloform reaction if the excess of KOCl is destroyed before acidification. With Br in AcOH, (I) gives 5-*bromoacetyl-*, m.p. 73—74°, and thence by KOAc in boiling EtOH 5-*acetoxyacetyl*-8-*methoxy*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 91—92°, hydrolysis of which did not give a pure $OH{\cdot}CH_2{\cdot}CO$ derivative. Structures are proved by conversion of (II) by S at 250° into 4 : 1-$OMe{\cdot}C_{10}H_6{\cdot}CO_2H$. R. S. C.

Phthaleins from phenol and naphthalene-1 : 2-dicarboxylic acid. M. H. Hubacher (*J. Amer. Chem. Soc.*, 1944, **66**, 255—256).—1 : 2-$C_{10}H_6(CO)_2O$, PhOH, and $SnCl_4$ at 113—116° give *phenol*-2 : 1- (I), 1 : 2-$C_{10}H_6$  O (22%), m.p. 291·1—292·4° (*diacetate*, m.p. 223·8—225·9°; *dipropionate*, m.p. 162·7—163·7°), and -1 : 2-*naphthalein* (II), 2 : 1-$C_{10}H_6$  O (5%), m.p. 267·5—269·5° (*diacetate*, m.p. 154·5—155·6°; *dipropionate*, m.p. 109·6—110°), converted by KOH at 240—245° into 2- and 1-$C_{10}H_7{\cdot}CO_2H$, respectively; the colour change (to magenta) occurs at pH ~8·6—10·5, but the colour given by (I) is ~4 times as intense as that given by (II); neither colour fades in dil. acid and that of (I) resists H_2O_2. M.p. are corr. R. S. C.

Derivatives of *cis*-3 : 6-*endo*methylene-Δ⁴-tetrahydrophthalic acid. M. S. Morgan, R. S. Tipson, A. Lowy, and W. E. Baldwin (*J. Amer. Chem. Soc.*, 1944, **66**, 404 407).—*cis*-3 : 6-*endo*Methylene-Δ⁴-tetrahydrophthalic anhydride (I) with H_2–Raney Ni in dioxan at 45°/2050 lb. gives 97% of the H_6-anhydride (II), m.p. 167·5—168°. The derived acids show each two well-defined breaks in the titration curve, whereas $(CH_2{\cdot}CO_2H)_2$ shows only one break and *o*-$C_6H_4(CO_2H)_2$ shows only a trace of the first break. In boiling MeOH, (I) and (II) give *Me H* cis-3 : 6-endo*methylene-Δ⁴-tetrahydro-*, m.p. 76—78·5°, and *-hexahydro-phthalate*, m.p. 77—79°, respectively. With a little *p*-$C_6H_4Me{\cdot}SO_2H$ in boiling ROH, (I) gives *Me*$_2$, b.p. 129—130°/9 mm. (indifferent to NH_3 at 0°), *Et*$_2$, b.p. 138—140°/8 mm., and *Bu*$^a_2$ cis-3 : 6-endo*methylene-Δ⁴-tetrahydrophthalate*, b.p. 174—176·6°/8 mm. With dry NH_3 at 170° or $(NH_4)_2CO_3$ at 200°, (I) gives the *imide* (III), m.p. 186·5—187°; (II) gives its *imide*, m.p. 174—175·5°, by the former method. With NH_2Ph in warm C_6H_6, (I) gives the *phenylimide*, m.p. 144°; in $CHCl_3$, (II) gives exothermally the anilic acid, m.p. 175—176° (decomp.), readily converted into the *phenylimide*, m.p. 152—153°. With *p*-toluidine in C_6H_6, (I) gives its p-*tolylimide*, m.p. 156·5—157°. With CH_2PhCl and NaOEt in boiling EtOH the imides give the unsaturated, m.p. 82·5—83·5°, and saturated *benzylimide*, m.p. 101—103°. In conc. aq. NH_3 at room temp. (I) or (II) gives *NH*$_4$ cis-3 : 6-endo*methylene-Δ⁴-tetrahydro-*, m.p. 172° (decomp.), and *-hexahydro-phthalamate*, m.p. 177° (decomp.), respectively, converted by aq. HCl at room temp. into the *phthalamic acids*, m.p. 136° (decomp.) and 165—166° (decomp.), respectively, which in boiling H_2O give *NH*$_4$ *H* cis-3 : 6-endo*methylene-Δ⁴-tetrahydro-*, m.p. 148° (decomp.) [derived $(NH_4)_2$ salt, m.p. indefinite], and *-hexahydro-phthalate*, m.p. 149—150°, respectively. An attempt to prepare the diamide from (III) by boiling conc. aq. NH_3 failed. With $AlCl_3$ in C_6H_6 at >45°, (II) gives 3-*benzoylnorcamphane-2-carboxylic acid* (87%), m.p. 170—171°, which gives no anthraquinone derivative in H_2SO_4 at 100°. R. S. C.

New synthesis of phenylpropaldehyde and its nuclear homologues. L. Bert (*Compt. rend.*, 1942, **215**, 356—357).—A benzenic hydrocarbon ArH is condensed directly (Friedel–Crafts) or, more generally, indirectly through MgArBr with $CH_2Cl{\cdot}CH{:}CHCl$ to $CH_2Ar{\cdot}CH{:}CHCl$, which is converted by cold Br or heated PCl_5 into $CH_2Ar{\cdot}CHBr{\cdot}CHClBr$ or $CH_2Ar{\cdot}CHCl{\cdot}CHCl_2$, respectively. Either of these when heated with NaOR (R = Me, Et, or Bu^a) gives $CHAr{:}CH{\cdot}CH(OR)_2$. Hydrogenation then gives $Ar{\cdot}[CH_2]_2{\cdot}CH(OR)_2$, hydrolysed to $Ar{\cdot}[CH_2]_2{\cdot}CHO$. No experimental results are recorded. H. W.

Complex behaviour of potassium permanganate towards an ethylenic function leading to a new mode of formation of *p-iso*propylphenylacetaldehyde. L. Bert (*Compt. rend.*, 1942, **215**, 276—277).—*p*-$C_6H_4Pr^\beta{\cdot}CH{:}CH{\cdot}CH_2{\cdot}OR$ (I) (R = Me, Et, Pr^a, Pr$^\beta$, Bu^a, Bu$^\beta$, *iso*-C_5H_{11}) is converted by agitation with a saturated aq. solution of $KMnO_4$ at room temp. into *p*-$C_6H_4Pr^\beta{\cdot}CH_2{\cdot}CHO$ (II) with some *p*-$C_6H_4Pr^\beta{\cdot}[CH{\cdot}OH]_2{\cdot}CH_2{\cdot}OR$. When R = Bu^a or *iso*-C_5H_{11} small amounts of Pr^aCO_2H or *iso*-$C_5H_{11}{\cdot}OH$, respectively, are also obtained. The course of the change is (I) + O → *p*-$C_6H_4Pr^\beta{\cdot}CHO$ (III) + $OR{\cdot}CH_2{\cdot}CHO$ (IV); (III) + (IV) (in presence of KOH from $KMnO_4$) → *p*-$C_6H_4Pr^\beta{\cdot}CH{:}C(OR){\cdot}CHO$ (V); (V) + O → *p*-$C_6H_4Pr^\beta{\cdot}CH{:}C(OR){\cdot}CO_2H$ → (−CO_2) *p*-$C_6H_4Pr^\beta{\cdot}CH{:}CH{\cdot}OR$ → (+H_2O) *p*-$C_6H_4Pr^\beta{\cdot}CH{:}CH{\cdot}OH$ + ROH → (II). No experimental results are recorded. H. W.

Substituted α-amylcinnamaldehydes. A. Weizmann (*J. Amer. Chem. Soc.* 1944, **66**, 310—311).—RCHO, *n*-$C_6H_{13}{\cdot}CHO$ (I), and piperidine in C_5H_5N at 100° give α-p-*anisylidene-*, b.p. 145°/0·3 mm. (*semicarbazone*, m.p. 143—145°), α-3 : 4-*dimethoxybenzylidene-*, b.p. 165°/0·6 mm. (*semicarbazone*, m.p. 175°), and α-3 : 4-methylenedioxybenzylidene-*n*-heptaldehyde, b.p. 158—159°/0·9 mm. (*semicarbazone*, m.p. 155°). PhCHO condenses more readily than do the above aldehydes. Vanillin and (I) do not react. R. S. C.

Reaction of maleic anhydride with aromatic oximes. G. La Parola (*Gazzetta*, 1943, **73**, 94—99; cf. A., 1937, II, 501).—$(CH{\cdot}CO)_2O$ (I) and α-*p*-tolualdoxime in C_6H_6 at the b.p. give N-p-*toluoylaspartic acid*, m.p. 182°. With α-anisaldoxime, (I) gives N-*anisoylaspartic*

acid, m.p. 180°. *α-p*-NMe_2·C_6H_4·CH:N·OH and *α*-piperonaldoxime give the nitriles, and *α*-salicaldoxime the aldehyde. E. W. W.

Spectroscopic study in the stereoisomeric capsanthin set. *cis*-Peak effect and configuration. A. Polgár and L. Zechmeister (*J. Amer. Chem. Soc.*, 1944, **66**, 186—190).—The fine structure of the absorption spectrum of capsanthin in hexane is obliterated by adding as little as 2% of EtOH and in abs. EtOH no structure at all is visible. 32 isomerides are possible, 5 of the ethylenic linkings being capable of *trans* → *cis* isomerisation. Isomerisation by I, insolation, and melting is investigated. Light is needed for development of a *cis*-peak. The customary considerations lead to the structures: neocapsanthin *A* 6-*cis*, *B* 5- or 7-*cis*, and *C* di-*cis*. R. S. C.

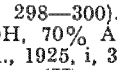
Isomerisation of aromatic ketones with aluminium chloride. G. Baddeley (*J.C.S.*, 1944, 232—236; cf. A., 1943, II, 264).—The isomerisations are of two types, viz., (*A*) those resembling the isomerisation of *o*-hydroxyaryl alkyl ketones, the mobile alkyl moving intramolecularly into the adjacent position, and (*B*) those involving migration (possibly intramol.) of the CO group. Migrations of alkyl in C_6H_6 homologues, phenols, aryl and hydroxyaryl ketones are related to one another, and to the Jacobson reaction. *o*-C_6H_4Me·COMe (*semicarbazone*, m.p. 212°) and $AlCl_3$ (2 mols.) at 170° for 1·5 hr. give *p*-C_6H_4Me·COMe (**I**) (85%) (type *B*) (*semicarbazone*, m.p. 208°), and no type *A* product. In presence of *m*-5-xylenol (**II**) at 160°, the yield of (**I**) is halved owing to formation of 2 : 4 : 5 : 1-OH·$C_6H_2Me_2$·COMe (**III**); the production of an acylating agent is thus possibly responsible for (**I**). *o*-C_6H_4Me·COEt similarly yields the *p*-isomeride (83%). 2 : 5 : 1-$C_6H_3Me_2$·COMe gives the 3 : 5 : 1-isomeride (77%) (*A*) (*semicarbazone*, m.p. 219°) and 8% of the 3 : 4 : 1-compound (**IV**) (*B*) [no (**IV**) is formed if (**II**) is present in the reaction mixture]. *o*-C_6H_4Et·COMe (*semicarbazone*, m.p. 182°) and $AlCl_3$ yield the *m*-isomeride (70%) (*A*) (*semicarbazone*, m.p. 175°) and a little of the *p*-compound (2 : 4-*dinitrophenylhydrazone*, m.p. 203°; *semicarbazone*, m.p. 191°). 2 : 5 : 1-$C_6H_3Et_2$·COMe (2 : 4-*dinitrophenylhydrazone*, m.p. 105°) yields the 3 : 5 :1-compound (83%) (*A*) (2 : 4-*dinitrophenylhydrazone*, m.p. 185°; *semicarbazone*, m.p. 149°), but no 3 : 4 : 1-isomeride (*semicarbazone*, m.p. 180°), thus showing the great mobility of Et. 2 : 4 : 1-$C_6H_3Me_2$·COMe (*semicarbazone*, m.p. 202°) and $AlCl_3$ or $AlBr_3$ (3 mols. at 150°) give 80% of (**IV**); $AlCl_3$ + (**II**) give (**III**) also. 2 : 4 : 6 : 1-$C_6H_2Me_3$·COMe and $AlCl_3$ afford the 3 : 4 : 5 : 1-isomeride (87%) (*A*) (*semicarbazone*, m.p. 217°) and 2 : 5 : 1-$C_6H_3Me_2$·COPh (at 190°) yields the 3 : 5 : 1-compound (90%) (*A*). *p*-Hydroxyacetophenones undergo isomerisations of type *B* only, and complete isomerisation of 4 : 2 : 1- into 2 : 4 : 1-OH·C_6H_3Me·COMe is achieved with slightly >1 mol. of $AlCl_3$. 2 : 5 : 1-$C_6H_3Me_2$·COMe is converted into the 2 : 4 : 1-isomeride by heating with 1 mol. of 6 : 3 : 4 : 1-OH·$C_6H_2Me_2$·COMe (1 mol.) and $AlCl_3$ (3 mols.); this is type *B* isomerisation occurring under conditions where there is no reagent capable of producing type *A*. 1-Keto-5 : 8-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene (**V**), b.p. 164°/20 mm. (*semicarbazone*, m.p. 222°), yields the 5 : 7-Me_2 compound (90%) (*A*) (*semicarbazone*, m.p. 245°), but 4 : 7-dimethyl-*α*-hydrindone (**VI**), m.p. 77°, is unchanged with $AlCl_3$. Ketones with no alkyl group *o*- to CO do not isomerise. All the *o*-alkylaryl ketones and (**V**), but not (**VI**), are hydrolysed by H_3PO_4 at 180°, CO being detached from the nucleus. The rigid and planar structure of (**VI**) suggests that the isomerisation of an aromatic ketone requires the propulsion of CO out of the plane of the aromatic nucleus. An explanation is given why isomerisation of type *A* is accelerated by alkyl *para* to the one which migrates. $AlBr_3$ (3 mols.) at 150° isomerises 6 : 2 : 4 : 1- to 2 : 4 : 5 : 1-OH·$C_6H_2Me_2$·COMe. $AlCl_3$ does not isomerise homologues of PhCN. The following are new: 3 : 5-*dimethylbenzophenone*, m.p. 70°; *semicarbazones*, m.p. 205°, 226°, and 143°, of *m*-C_6H_4Me·COMe, 1-keto-1 : 2 : 3 : 4-tetrahydronaphthalene, and *p*-$C_6H_4Pr^{\alpha}$·COEt (**VII**), respectively; (**VII**) and 2 : 5 : 1-$C_6H_3Pr^{\alpha}_2$·COMe give 2 : 4-*dinitrophenylhydrazones*, m.p. 147° and 75°, respectively. A. T. P.

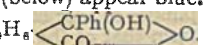
Factors determining the course and mechanism of Grignard reactions. XIII. Effect of metallic halides on the reaction of sterically hindered acid halides with magnesium methyl iodide. M. S. Kharasch, R. Morrison, and W. H. Urry (*J. Amer. Chem. Soc.*, 1944, **66**, 368—371; cf. A., 1944, II, 215).—Adding MesCOCl (Mes = mesityl) to MgMeI gives good yields of COMeMes, but the reverse addition gives 25% of COMeMes and 50% of $(MesCO)_2$ (cf. Fuson *et al.*, A., 1938, II, 445). Use of very pure Mg or allowing the MgMeI solution to age increases the proportion of COMeMes, as also does addition of 1 atom-% of Cu or, better, 1 mol.-% of $MnCl_2$, $FeCl_3$, or CuCl. MgMeBr gives 87% of COMeMes, but addition of $CoCl_2$ leads to much $(MesCO)_2$, an effect shown less markedly with MgMeI. A free radical chain mechanism is proposed. R. S. C.

Acetylation of 1 : 2-dimethylnaphthalene. P. A. Plattner and A. Ronco (*Helv. Chim. Acta*, 1944, **27**, 400—403).—1 : 2-$C_{10}H_6Me_2$, b.p. 135—137°/13 mm. (picrate, m.p. 129—130°), is obtained homogeneous (76% yield) by the successive action of Li and Me_2SO_4 on 2 : 1-$C_{10}H_6MeBr$ in Et_2O. It is converted by AcCl and $AlCl_3$ in CS_2 or $PhNO_2$ into 3 : 4-*dimethyl*-1-*naphthyl Me ketone* (**I**), b.p. 135—137°/0·3 mm. (*picrate*, m.p. 134—135°; *semicarbazone*, m.p. 225°). The constitution of (**I**) is established by its oxidation (NaOBr) to 3 : 4-*dimethyl*-1-*naphthoic acid*, m.p. 226—227° (*Me* ester, m.p. 49°), also obtained by converting 4 : 1 : 2-$C_{10}H_5BrMe_2$ by CuCN at 260° into 3 : 4-*dimethyl*-1-*naphthonitrile*, m.p. 120—121°, and subsequent hydrolysis with boiling 25% KOH–EtOH. M.p. are corr. H. W.

Molecular rearrangements of phenyl styryl ketone oxides. J. Algar and J. McKenna (*Proc. Roy. Irish Acad.*, 1944, **49, B**, 225—249).—COAr·CH:CHAr′ with H_2O_2–aq. EtOH–NaOH gives the oxide, which is rearranged by 50% H_2SO_4 at room temp. into COAr·CHAr′·CHO. This is converted into the corresponding pyrazole by EtOH–NHPh·NH_2. The following are described: *Ph* 3 : 4-*dimethoxystyryl ketone oxide*, m.p. 87—89°; *o*-, m.p. 114—115°, and p-*anisyl* p-*methoxystyryl ketone oxide*, m.p. 119—121°; o-*anisyl* 3 : 4-*methylenedioxystyryl ketone oxide*, m.p. 151°; *α-phenyl-β*-p-*anisylpropane-αγ-dione*, m.p. 115° (uncorr.); *α-phenyl-β*-3 : 4-*methylenedioxyphenylpropane-αγ-dione*, m.p. 108—109°; *α-phenyl-β*-3 : 4-*dimethoxyphenylpropane-αγ-dione*, m.p. 113—114°; *α-phenyl-β*-o-*anisylpropane-αγ-dione* (an oil; Cu salt, m.p. 190—195°, softening at 185°); *β-phenyl-α*-p-*anisylpropane-αγ-dione*, m.p. 82—84° (uncorr.); *αβ-di*-p-*anisylpropane-αγ-dione*, m.p. 135—136°; *β-phenyl-α*-o-*anisylpropane-αγ-dione* (**I**) [an oil; *Cu* salt (+EtOH), m.p. 243° (decomp.), softening at 240°]; *α*-o-*anisyl-β*-p-*anisylpropane-αγ-dione* [an oil; *Cu* salt m.p. 221—222° (decomp.), softening at 214°]; *α*-o-*anisyl-β*-3 : 4-*methylenedioxyphenylpropane-αγ-dione* [an oil; *Cu* salt m.p. 275°)(uncorr.; decomp.)]; *α*-o-*anisyl-β*-3 : 4-*dimethoxyphenylpropane-αγ-dione*; *β-phenyl-α*-2 : 4-*dimethoxyphenylpropane-αγ-dione* (**II**) [an oil; *Cu* salt (+EtOH), m.p. 200—210° after softening]. 1 : 5-*diphenyl*-4-p-*anisyl*-, m.p. 150—151°, -4-3′ : 4′-*methylenedioxyphenyl*-, m.p. 199°, and -4-3′ : 4′-*dimethoxyphenyl*-, m.p. 163°, 1 : 4-*diphenyl*-5-p-*anisyl*-, m.p. 183°, and 1-*phenyl*-4 : 5-*di*-p-*anisyl-pyrazole*, m.p. 173°. Small yields of *iso*flavone and 7-hydroxy*iso*flavone are obtained from (**I**) and (**II**), respectively, by $AlBr_3$ in boiling C_6H_6. Prolonged refluxing of (**I**) gives a *compound*, m.p. 147·5—148·5°, probably *o*-OH·C_6H_4·CO·CPh:CHPh. M.p. are corr. except where stated. J. H. Ba.

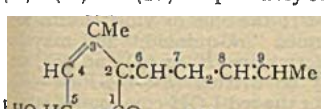
Functional aptitude of the methyl group. VIII. Formation of anilides by the action of nitroso-derivatives on compounds with an active methyl group. L. Chardonnens and P. Heinrich (*Helv. Chim. Acta*, 1944, **27**, 321—332; cf. A., 1940, II, 160).—Certain secondary products of the condensation of activated Me groups with NO-compounds are shown to be anilides and not nitrones. 3 : 4 : 1-NO_2·C_6H_3Me·COPh and *p*-NO·C_6H_4·NMe_2 afford 2-nitro-4-benzoylbenzaldehyde-*p′*-dimethylaminoanil, m.p. 174—175°, and 3-*nitrobenzophenone*-4-*carboxy*-p-*dimethylaminoanilide* (**I**), m.p. 217°. Similarly PhNO yields 3-*nitrobenzophenone*-4-*carboxyanilide* (**II**), m.p. 169°. 2-Nitro-4-benzoylstilbene is oxidised (CrO_3 in AcOH) to 3-nitrobenzophenone-4-carboxylic acid (*Me* ester, m.p. 82°), the chloride of which with NH_2Ph (or *p*-NMe_2·C_6H_4·NH_2) in C_5H_5N affords (**I**) [or (**II**)]. The minor compound from 3 : 3′-dinitro-4-methylbenzophenone (**III**) and *p*-NO·C_6H_4·NMe_2 is 3 : 3′-*dinitrobenzophenone*-4-*carboxy*-p-*dimethylaminoanilide* (**IV**), m.p. 234° (cf. A., 1939, II, 428); the *-anilide* (**V**), m.p. 190°, is obtained similarly from PhNO. (**III**) and PhCHO in presence of piperidine afford trans(?)-3 : 3′-*dinitro*-4-*styrylbenzophenone*, m.p. 168°, also obtained from the isomeride, m.p. 155—156°, by the action of a little I in boiling $PhNO_2$; it is oxidised by CrO_3 in AcOH at 70° to 3 : 3′-*dinitrobenzophenone*-4-*carboxylic acid*, m.p. 193—194°, also obtained from (**III**) and HNO_3 (*d* 1·15) at 155—165°; it is converted through its chloride into the *Me* ester, m.p. 124°, (**IV**), and (**V**). 2-Nitro-4-benzoylbenzaldehyde and NHPh·OH in boiling EtOH afford the N-*Ph* derivative, m.p. 136°, of 2-nitro-4-benzoylbenzaldoxime, isomerised by calcined Na_2CO_3 in boiling EtOH to (**II**). 2-Nitro-4-*m*-nitrobenzoylbenzylidene-*p*-dimethylaminoanil in C_6H_6 is hydrolysed by aq. HCl to 2-*nitro*-4-m-*nitrobenzoylbenzaldehyde*, m.p. 142·5° [*phenylhydrazone*, m.p. 218·5° (decomp.)], converted by NHPh·OH into the N-*Ph* derivative, m.p. 157°, of 2-nitro-4-*m*-nitrobenzoylbenzaldoxime which is isomerised by Na_2CO_3 in boiling EtOH to (**V**). The N-*Ph* derivative, m.p. 147·5°, of 2-nitro-4-benzeneazobenzaldoxime is similarly isomerised to 3-nitroazobenzene-4-carboxyanilide. 5-Nitrobenzophenone-2-carboxylic acid [from 5 : 2 : 1-NO_2·C_6H_3Me·CO_2Ph (**VI**) and HNO_3 (*d* 1·15) at 160—170°] is converted ($SOCl_2$) into the chloride and thence into the *p*-dimethylaminoanilide, m.p. 240°, identical with the substance derived from *p*-NO·C_6H_4·NMe_2 and (**VI**), which, therefore, is not a nitrone. H. W.

Normal and *ψ*-structures of 8-benzoyl-1-naphthoic acid and derivatives. H. E. French and J. E. Kircher (*J. Amer. Chem. Soc.*, 1944, **66**, 298—300).—Crystallisation of 8 : 1-$C_{10}H_6Bz$·CO_2H (*A*) from EtOH, 70% AcOH, or $CHCl_3$ gives a form (**I**), m.p. 110° (Mason, A., 1925, i, 33, 34), but from xylene, *cyclo*hexane, or PhMe gives a form (**II**), m.p. 129—130° (Knapp, A., 1936, 726). After heating at 90°, (**I**) gives a form, m.p. 154°. (**I**) or (**II**) in $CHCl_3$ or (**II**) after boiling in *cyclo*hexane has absorption max. at 3081—3120 and 3252—3297 A., thus resembling 8 : 1-$C_{10}H_6$  O (**III**) (max. at 3092 and 3275 A.) but not 1 : 8-$C_{10}H_6Bz_2$ (max. at 2190 A.). (**III**), its ditolyl analogue, and 1 : 8-$C_{10}H_6(CO)_2O$ show a blue

fluorescence in ultra-violet light, but (**VI**) and (**VII**) (below) appear greyish-white; (*A*), its toluoyl analogue, and (**V**) (below) appear blue. Thus, (*A*) exists in solution largely as 8 : 1-$C_{10}H_6$ 

With $SOCl_2$, (**I**) gives a product which by crystallisation from C_6H_6 gives *α-chloro-α-phenyl*-1 : 8-*naphthalide* (**IV**), m.p. 125—127° (absorption max. at 2961, 3074, and 3251 A.), converted by EtOH into the *α-OEt*-compound (*Et* 8-*benzoyl*-1-*naphthoate ψ*-ester) (**V**), m.p. 166° (absorption max. at 3085 and 3259 A.) (cf. Mason, *loc. cit.*). The Ag salt of (*A*) with EtI gives *Et* 8-*benzoyl*-1-*naphthoate* (normal form) (**VI**), m.p. 134° [absorption max. at 2946 A.; cf. 1 : 8-$C_{10}H_6(CO_2Et)_2$ (**VII**), max. at 2950 A.]. (**V**) and (**VI**) are separated by chromatography (Al_2O_3; C_6H_6–light petroleum), whereby it is proved that crude (**V**), prepared from (**IV**), contains some (**VI**). The crude oily chloride from (**I**) reacts with EtOH more readily than does pure (**IV**) and gives mainly (**VI**); the crude product thus contains much 8 : 1-$C_{10}H_6Bz$·COCl. With C_6H_6–$AlCl_3$, (**IV**) gives 25—50% of (**III**); the oily chloride gives HCl and tars. R. S. C.

Structure of pyrethrolone and related compounds. II. T. F. West (*J.C.S.*, 1944, 239—242; cf. A., 1944, II, 136).—(+)-Pyrethrolone (**I**) with Me_2SO_4–Et_2O–KOH gives a Me ether (**II**), b.p. 87°/0·3 mm., $[\alpha]_D^{20}$ +97·3° in EtOH [regenerated from its semicarbazone (**III**), m.p. 183—184°, $[\alpha]_D^{20}$ −82° in C_5H_5N, by aq. $KHSO_4$–Et_2O], whereas the semicarbazone, m.p. 208°, of (**I**) with MeOH–H_2SO_4 yields *dl*-pyrethrolone Me ether (**IV**), b.p. 85°/0·2 mm. (semicarbazone, m.p. 196—197°, $[\alpha]_D$ ±0° in C_5H_5N). (**III**) with Me_2SO_4–H_2SO_4 gives (**IV**). (**II**) and (**IV**) are probably stereoisomeric; neither is reducible by the Ponndorf–Meerwein method. An explanation for the failure of derivatives of (**I**) to undergo Diels–Alder condensation (cf. LaForge, *et al.*, A., 1938, II, 372) is based on the postulation of a *cis*-configuration for the pentadienyl side-chain. A new formulation (*A*) for (**I**) is proposed. A. T. P.



Preparation of substituted *cyclo*pentanones. Catalytic hydrogenation of (III) αβ-unsaturated carbonyl compounds, (IV) 2 : 3-diphenyl-Δ²-*cyclo*pentenone. H. A. Weidlich and M. Meyer-Delius (*Ber.*, 1941, **74**, [*B*], 1195—1212, 1213—1218).—III. Catalytic hydrogenation of C:C·CO in acid is an ionic reaction, occurring by 1 : 2-addition to the C:C or C:O; in alkaline solution the reaction is at. and occurs by 1 : 4-addition. Hydrogenations listed below are by H_2–PdO_2 in EtOH; " acid " and " alkali " denote addition of a little conc. HCl or KOH–EtOH, respectively. In alkali CHPh:CH·COPh gives Ph·$[CH_2]_2$·COPh (100%) and in acid gives $[CH_2]_3Ph_2$ (100%). Reduction of CHPh:CH·CHO in alkali becomes very slow after absorption of 1 H_2 and a good yield of Ph·$[CH_2]_2$·CHO is obtained (cf. lit.). 4-Hydroxy-3 : 4-diphenyl-Δ³-*cyclo*pentenone (anhydroacetonebenzil), m.p. 146—147°, b.p. 190°/0·4 mm. [2 : 4-*dinitrophenylhydrazone*, m.p. 262° (decomp.)], in alkali absorbs 1 H_2, giving a partly dehydrated mixture, whence by dehydration in boiling AcOH, 3 : 4-diphenyl-Δ³-*cyclo*pentenone (**I**), m.p. 108—109° [*semicarbazone*, m.p. 219° (decomp.); 2 : 4-dinitrophenylhydrazone, m.p. 252° (lit. 259—260°) (decomp.)], is obtained; in acid ~2·5 H_2 are absorbed, yielding (**I**) and 1 : 2-*diphenyl*-Δ¹-cyclo*pentene*, b.p. 119°/0·4 mm., the structure of which is proved by oxidation to *αε-diphenyl*-n-*pentane-αε-dione*, m.p. 64·5—65°. In alkali or acid (**I**) yields only *cis*-3 : 4-diphenyl-*cyclo*pentanone, m.p. 106°. Dimerisation during hydrogenation occurs by way of C·CH:C·OH which either adds 1 H or dimerises, and will thus occur only when reduction is slow, *i.e.*, in alkaline solution; thus, $CO(CH{:}CHPh)_2$ in acid gives $CO([CH_2]_2{\cdot}Ph)_2$ (2 : 4-*dinitrophenylhydrazone*, m.p. 115—117°) and OH·CH($[CH_2]_2$·Ph)$_2$, but in alkali gives Ph·$[CH_2]_2$·CO·CH:CHPh and (CHPh:CH·CO·CH$_2$·CHPh)$_2$. The steric course of reduction may be predicted in simple cases: 1 : 2-addition in acid resembles simple hydrogenation of an isolated C:C and leads to the energy-richer *cis*-form; 1 : 4-addition in alkali leads to CH·C:C·OH, ketonisation of which leads to the energy-poorer *trans*-form. *E.g.*, 3-*β*-naphthyl-Δ²-*cyclo*pentenone-2-acetic acid (as Me ester) in alkali rapidly absorbs 1 H_2 to yield cis-3-*β-naphthyl*cyclo*pentanone*-2-*acetic acid*, m.p. 106°, b.p. 192°/0·3 mm., the *trans*-form of which was obtained by Koebner *et al.* (A., 1939, II, 75) by H_2–Pd–$SrCO_3$; their *x*-norequilenin was similarly a *trans*-form. Cyclisation of $[CH_2]_4Bz_2$ gives 2-benzoyl-1-phenyl*cyclo*pentanol (**II**) and thence 1-benzoyl-2-phenyl-Δ²- (**III**), m.p. 97° (2 : 4-*dinitrophenylhydrazone*, m.p. 132—140°), and -Δ¹-*cyclo*pentene (**IV**), m.p. 42° (2 : 4-*dinitrophenylhydrazone*, m.p. ~165—170°) (cf. Bauer, A., 1914, i, 701). (**II**) is a mixture; *trans*-elimination of H_2O from the *trans*-form gives (**IV**), whereas (**III**) is derived from *cis*-(**II**). In alkali, (**III**) or (**IV**) gives only trans-2-*benzoyl*-1-*phenyl*cyclo*pentane*, m.p. 75—76° (2 : 4-*dinitrophenylhydrazone*, m.p. 129—130°), but in acid gives cis-1-*phenyl*-2-*α-hydroxybenzyl*cyclo*pentane*, m.p. 104—106°, oxidised by CrO_3 to cis-1-*phenyl*-2-*benzoyl*cyclo*pentane*, m.p. 42—43° (2 : 4-*dinitrophenylhydrazone*, m.p. 132—134°).

IV. Hydrogenation of 2 : 3-diphenyl-Δ²-*cyclo*pentenone (**V**) in alkaline EtOH in presence of Pd gives *trans*-2 : 3-diphenyl*cyclo*pentanone (**VI**), m.p. 97° (*semicarbazone*, m.p. 192°) (cf. Burton *et al.*, A., 1939, II, 567), but in EtOH + 1 drop of conc. HCl gives *cis*-1 : 2-diphenyl*cyclo*pentane (**VII**), (**VI**), and, sometimes, trans-trans-2 : 3-*diphenyl*cyclo*pentanol* (**VIII**), m.p. 110—112° [oxidised by CrO_3–AcOH to (**VI**)]. The alkaline reduction and formation of (**VII**) in acid conforms to the rules laid down above; formation of

(**VI**) and (**VIII**) in acid is due to hindrance by the 2 Ph slowing reaction so that 1 : 4-addition occurs. In presence of $CH(OEt)_3$, addition to the O is largely prevented and hydrogenation in acid gives, by way of the ketal, cis-2 : 3-*diphenyl*cyclo*pentanone*, m.p. 71° (*semicarbazone*, m.p. 189—190°), as well as some (**VI**). In presence of PtO_2 in acid, (**V**) gives trans-cis-2 : 3-*diphenyl*cyclo*pentanol* (**IX**), b.p. 142—144°/0·3 mm., oxidised to (**VI**) by CrO_3–AcOH. R. S. C.

Dehydrogenation of *cyclo*hexanols [to *cyclo*hexanones].—See B., 1944, II, 156.

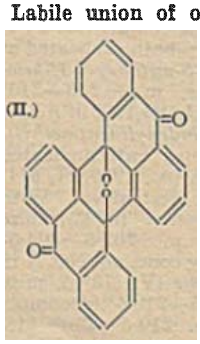
Derivatives of 5-methoxyhydrindene and 6-methoxy-1 : 2 : 3 : 4-tetrahydronaphthalene. Synthesis of β-2-carboxy-5-methoxyphenylpropionic acid. W. S. Johnson, J. M. Anderson, and W. E. Shelberg (*J. Amer. Chem. Soc.*, 1944, **66**, 218—222).—*m*-OH·C_6H_4·CHO, $CH_2(CO_2H)_2$, and a little piperidine in C_5H_5N at 100° give *m*-OH·C_6H_4·CH:CH·CO_2H, m.p. 194—195°, hydrogenated (PtO_2; MeOH) to *m*-OH·C_6H_4·$[CH_2]_2$·CO_2H, m.p. 111·8—112·5°, which in HF gives 5- (85%) (**I**), m.p. 184—185·5° [semicarbazone, m.p. 222—222·5° (decomp.; bath preheated at 215°); *acetate*, m.p. 92·8—93·2°], and 7-hydroxy-1-hydrindone (13%), m.p. 110·5—111·5°. Me_2SO_4–alkali converts (**I**) into the Me ether (**II**), m.p. 110—110·5° [semicarbazone, m.p. 240—241° (decomp.); 2 : 4-*dinitro*-, m.p. 282—284° (decomp.; uncorr.), and *p-nitro-phenylhydrazone*, m.p. 209—211·5° (decomp.; bath preheated at 200°)], which is also obtained in 78% yield from 5-methoxyhydrindene by CrO_3 in AcOH–H_2O at 5—10° and then room temp. With NaOMe and HCO_2Et in C_6H_6–N_2, (**II**) gives 5-*methoxy*-2-*hydroxymethylene*-1-*hydrindone* (**III**) (98%), m.p. 138—138·5° (decomp.) (purple $FeCl_3$ colour) [*bis*-2 : 4-*dinitrophenylhydrazone*, m.p. 223—226° (decomp.; bath preheated at 220°)], which at 140—150° gives HCO_2H and 5-*methoxy*-2-1′-*keto*-5′-*methoxy*-2′-*hydrindenylidenemethyl*-1-*hydrindone*, m.p. 213—215° (decomp.; bath preheated at 205°), and with NH_2OH,HCl in AcOH at room temp. gives *di*-(1-*keto*-5-*methoxy*-2-*hydrindenylidenemethyl*)-*hydroxylamine* (**IV**) (90%), m.p. 216—218° (decomp.; bath preheated at 214°). The supposed nitrile of Robinson *et al.* (A., 1939, II, 511) is probably a similar bimol. hydroxylamine derivative. With Br–Et_2O, (**II**) gives 2-*bromo*-5-*methoxy*-1-*hydrindone* (95%), m.p. 107·8—108·5° [2 : 4-*dinitrophenylhydrazone*, m.p. 202·5—204·5° (decomp.; bath preheated at 195°)], converted by conc. aq. NaCN in boiling EtOH into 2-*cyano*-5-*methoxy*-1-*hydrindone* (**V**) (73%), m.p. 96—96·5° [2 : 4-*dinitrophenylhydrazone*, m.p. 217·5—219·5° (decomp.; bath preheated at 215°); *semicarbazone*, m.p. 219·5—220° (decomp.; bath preheated at 214°)], which could not be obtained from (**III**) or (**IV**). 6-Methoxy-1 : 2 : 3 : 4-tetrahydronaphthalene and $Pb(OAc)_4$ in AcOH at room temp. give exothermally (cooling required) 1-*acetoxy*-6-*methoxy*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (62%), b.p. 118·5°/0·5 mm., which is unstable, particularly in presence of traces of acid, and with a little $KHSO_4$ at 120° rapidly gives AcOH and 7-*methoxy*-1 : 2-*dihydronaphthalene* (**VI**), b.p. 94—95°/2—3 mm. 48% HBr converts (**VI**) into a *dimeride* (? 7-*methoxy*-3-6′-*methoxy*-1′ : 2′ : 3′ : 4′-*tetrahydro*-1′-*naphthyl*-1 : 2-*dihydronaphthalene*), m.p. 75·5—76·5°, supposed by Long *et al.* (A., 1942, II, 96, m.p. 73—74°) to be (**VI**). *β-2-Carboxy*-5-*methoxyphenylpropionic acid*, m.p. 203·5—204°, is obtained from (**IV**) by boiling 2% aq. NaOH (61% yield), from (**V**) by boiling 5% KOH (88% yield), and from (**VI**) by $KMnO_4$ in $COMe_2$ at 0—3° and then room temp. (40% yield), and is cyclised to (**II**) by distilling with BaO. Unless otherwise stated, m.p. are corr. R. S. C.

Introduction of the angular methyl group. II. *cis*- and *trans*-8-Methyl-1-hydrindanone. W. S. Johnson (*J. Amer. Chem. Soc.*, 1944, **66**, 215—217; cf. A., 1943, II, 330).—*cis*-1-Keto-2-benzylidene-9-methyldecahydronaphthalene (**I**) with $KMnO_4$ (excess) in $COMe_2$ at 2—4° and then 0° gives crude *β*-2-carboxy-2-methyl*cyclo*hexylpropionic acid, m.p. 99·5—103°, converted by distillation with BaO at 300—320° into *cis*-8-methyl-1-hydrindanone, m.p. 34·5—36°, b.p. 106°/20 mm. (oxime, m.p. 87—88°; 2 : 4-*dinitrophenylhydrazone*, m.p. 140·5—141°), which only slowly gives the semicarbazone, m.p. 224·5—225·5° (decomp.) (cf. lit.). The *trans*-isomeride of (**I**) gives similarly trans-*β*-2-*carboxy*-2-*methyl*cyclo*hexylpropionic acid*, m.p. 179—180°, and thence *trans*-8-methyl-1-hydrindanone, b.p. 109°/20 mm. (oxime, m.p. 115—115·5°; 2 : 4-*dinitrophenylhydrazone*, m.p. 146·5—147°, resolidifies, remelts 153·5—154°), which readily forms the semicarbazone, m.p. 242—243° (decomp.) (cf. lit.). M.p. are corr. R. S. C.

Synthesis of 5-hydroxy-1-keto-6 : 7-dimethoxy-3-ethyl-1 : 2 : 3 : 4-tetrahydronaphthalene. K. Wallenfels (*Ber.*, 1941, **74**, [*B*], 1428—1433).—2 : 3 : 4 : 1-$(OMe)_3C_6H_2$·CHO (**I**) (improved prep.), b.p. 161—163°/10 mm., $(Pr^aCO)_2O$, and Pr^aCO_2K at 180° give 2 : 3 : 4-*trimethoxy-α-ethylcinnamic acid* (**II**), m.p. 117°. CHEtBr·CO_2Et, (**I**), Zn, and a trace of I in boiling C_6H_6 give an Et ester, m.p. 62°, b.p. 176—177°/3 mm., hydrolysed to (**I**) by boiling 10% KOH–EtOH. H_2–Pd–$BaSO_4$ reduces (**II**) in AcOH to α-2 : 3 : 4-*trimethoxybenzyl*-n-*butyric acid*, b.p. 156—157°/0·05 mm., which with boiling $SOCl_2$–C_6H_6 gives the acid chloride and thence the oily CHN_2-ketone. With Ag_2O–MeOH at 50° and then the b.p. this gives the Me ester, b.p. 128—130°/0·1 mm., hydrolysed by boiling 2N-NaOH to β-2 : 3 : 4-*trimethoxybenzyl*-n-*valeric acid*, b.p. 152—153°/0·05 mm., which with $SOCl_2$–light petroleum and then $SnCl_4$–C_6H_6 gives 1-*keto*-5 : 6 : 7-*trimethoxy*-, b.p. 121—122°/0·05 mm., or with $AlCl_3$ in CS_2 at 0° and then the b.p. gives 5-*hydroxy*-1-*keto*-6 : 7-*dimethoxy*-3-*ethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (**III**), m.p. 115°. With SeO_2 in AcOH or EtOH, (**III**) gives a red dye, 1 : 3 : 2 : 5 : 6 : 7 : 4-O:C_{10}HEt(OH)$_2$(OMe)$_2$:O (absorption max. at 553 mμ.), sol. in $NaHCO_3$ with a violet and in NaOH with a blue colour, reduced by $Na_2S_2O_4$ to the colourless quinol and converted by CH_2N_2 into the lighter-coloured $(OMe)_4$-quinone, insol. in $NaHCO_3$ or NaOH, which in boiling, dil. HCl gives 1 : 3 : 5 : 2 : 6 : 7 : 4-O:C_{10}HEt(OH)(OMe)$_3$:O, insol. in $NaHCO_3$, but sol. in NaOH with a red colour. R. S. C.

Ketones, ketonic acids, and enol-lactones. IV. *cyclo*-**Pentane-1 : 3-diones.** P. Ruggli and J. Schmidlin (*Helv. Chim. Acta*, 1944, **27**, 499—502).—2 : 4-Diphenyl*cyclo*pentane-1 : 3-dione (**I**), m.p. 204—205°, has been obtained by a second method (cf. Eskola, *Diss., Helsinski*, 1937). Like other supposedly *cyclo*pentane-1 : 3-diones, it possesses unusual properties which may be proper to these compounds or indicative of a different structure. $CO(CH_2Ph)_2$ and $Et_2C_2O_4$ give 3 : 5-diphenyl*cyclo*pentane-1 : 2 : 4-trione, m.p. 190—192°, hydrogenated (Raney Ni–EtOH at 50°) to 5-*hydroxy*-2 : 4-*diphenyl*cyclo*pentane*-1 : 3-*dione* (**II**), m.p. 173—175° (decomp.), which dissolves in cold Na_2CO_3 and is converted by Ac_2O–C_5H_5N at room temp. into a *diacetate*, m.p. 114·5—115·5°. Dehydration of (**II**) in anhyd. glycerol at 185—190° leads to 3 : 4-*diphenyl*-Δ^4-cyclo*pentene*-1 : 3-*dione*, m.p. 146—146·5°, which dissolves in warm dil. NaOH, does not give a colour with $FeCl_3$, and is hydrogenated (Raney Ni in C_6H_6 at room temp.) to (**I**). H. W.

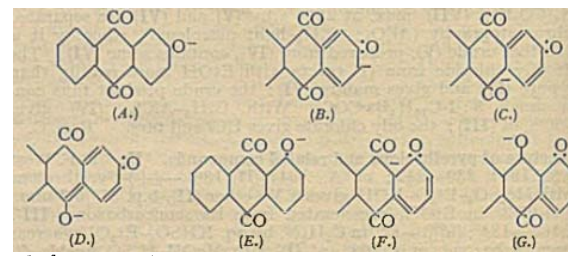
Labile union of oxygen to carbon. Photo-oxidation of *hetero*-coerdianthrone. C. Dufraisse and M. T. Mellier (*Compt. rend.*, 1942, **215**, 541—543).—Irradiation of *hetero*coerdianthrone (7′ : 7″) (**I**) (in CS_2) causes rapid oxidation with disappearance of the violet colour, and formation of the photo-oxide (**II**) (cf. Scholl *et al.*, A., 1932, 617), reconverted into (**I**), with evolution of O_2, at 150°. In C_5H_5N (6 hr.), followed by heating with C, (**I**) yields (**II**) and the 9 : 10-dihydroxy-9 : 10-dihydro-derivative (**III**). Colourless solutions of (**II**) in C_5H_5N in sunlight become similar in colour to that observed with (**I**) in C_5H_5N. Change of solvent and use of C partially transforms (**II**) into (**III**); after irradiation of (**I**) in C_5H_5N for 3 min., (**II**) is formed but is more difficult to purify. A. T. P.



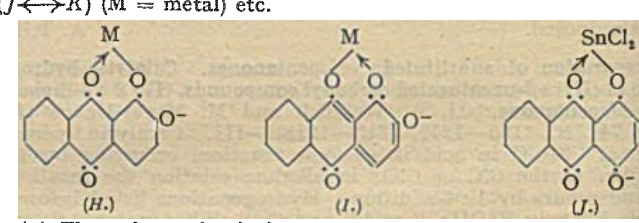
Substituted naphthaquinones.—See B., 1944, II, 197.

Optically active α-phylloquinone (vitamin-K_1). P. Karrer, H. Simon, and E. Zbinden (*Helv. Chim. Acta*, 1944, **27**, 317—319).—α-Phylloquinone (**I**), obtained by condensation of 2 : 1 : 4-$C_{10}H_5Me(OH)_2$ with natural phytol and anhyd. $H_2C_2O_4$ in dioxan followed by Ag_2O in Et_2O + Na_2SO_4, has $[\alpha]_D^{20}$ 0·4°±0·04° in C_6H_6. Dihydro-α-phylloquinone diacetate, obtained from (**I**) and Zn dust in Ac_2O–C_5H_5N, has $[\alpha]_D^{20}$ ~+1·5° to +1·65° or ~1·8° in EtOH, when derived from phytol with $[\alpha]_D$ +0·06° or +0·2°. H. W.

(A) **Structure of hydroxyanthraquinones in their salts. Homopolar (pseudo-)ammonium salts. Mesomerism.** (B) **Formation of [substituted] ammonium salts in solution in their basic components and of metal complex salts with ammonia and amines.** R. Scholl [(A) with P. J. Dahll]. (C) **Structure of anthraquinol-1-carboxylactones and their salts.** R. Scholl, K. Meyer, and C. Seer (*Ber.*, 1941, **74**, [*B*], 1129—1170, 1171—1181, 1182—1189).—(A) *Salts* are prepared containing: 1-hydroxyanthraquinone and 1 mol. of NH_3, NH_2R (R = Me, Et, and Pr^a here and below), $NHMe_2$ and $NHEt_2$; 2-hydroxyanthraquinone and 1 mol. of NH_3, NH_2R, NHR_2, NMe_3, NEt_3, and 1-ethylpiperidine (**I**); alizarin and 1 mol. of NH_3, NH_2Et, NH_2Pr^a, NHR_2, NMe_3, NEt_3, (**I**), and C_5H_5N, or 2 mols. of NH_3 and NH_2Me; hystazarin with 2 mols. of NH_3 and piperidine; quinizarin and 1 mol. of NH_3, NH_2Et, NH_2Pr^a, $NHMe_2$, or $NHEt_2$, or 2 mols. of NH_2Me; anthrarufin and 1 mol. of NH_3 or 2 mols. of NH_2R; anthraflavin and 1 mol. of $NHPr^a_2$, NMe_3, NEt_3, or (**I**), and 2 mols. of NH_3, NH_2R, or NHR_2; purpurin and 1 mol. of NHR_2, NR_3, or (**I**), 2 mols. of NH_3, NH_2Et, or NH_2Pr^a, 2·5 mols. of NH_3, or 3 mols. of NH_2Me; when no salt is recorded in these series, none could be obtained. Prep. was by gaseous NH_3 or by an excess of the liquid amine at room temp. or 20° above its b.p. Colours of the salts are of three types, yellow to orange-red or brown, pink to red, or bluish-violet to blue. Colour in solution often differs from that of the solid and light-coloured solids (or base-free anthraquinone) often separate from dark-coloured solutions. The colour of solutions is often reversibly changed by addition of a second solvent. The depth of colour and tendency to salt-formation decrease for any one anthraquinone from primary through *sec.* to *tert.* bases; salt-formation thus involves linkings R·O·H⋖–NR_3. Differences in colour are due to existence of the separate mesomeric forms, *e.g.*, the series (*A*)–(*B*)–(*C*)–(*D*) and (*E*)–(*F*)–(*G*); these are

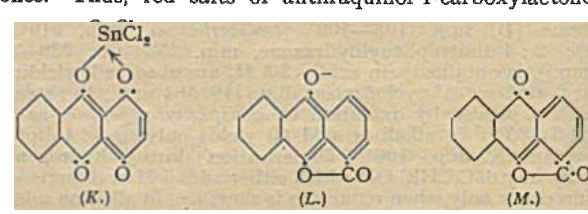


termed electrotropic forms. Salts, solid or in solution, may exist as equilibria with one form largely preponderating. The yellow-orange forms are wholly or mostly the "*el.*-benzoid" form (*A*), (*E*), etc., and may be written, *e.g.*, (*A*⋖⋗*B*); the blue or violet forms are mainly or wholly (*D*), (*G*), etc., termed "*el.*-quinoid," and may be written (*A*⋖⋗⋗*D*) etc.; the red forms are (*B*) or (*C*) and (*F*), are termed "*el.*-carbeniates," and may be written (*E*⋖⋗⋗⋗*F*⋖⋗*G*) etc.; decision between (*B*) and (*C*) for the red 1-OH-compounds is impossible. Metal lakes are similarly considered to be, *e.g.*, (*H*⋖⋗*I*), (*J*⋖⋗*K*) (M = metal) etc.



(B) The colour of solutions of hydroxyanthraquinones in bases or mixed bases is used to determine the "activity" of the bases. These activities are in the same qual. order as the dielectric consts. so long as the latter do not vary greatly.

(C) Salts of anthraquinol-1-carboxylactones which are capable of electropism in the way outlined above are orange, red, or blue according to the nature of the base, solvent, or mixture of solvents; their general colour behaviour resembles that of hydroxyanthraquinones. Thus, red salts of anthraquinol-1-carboxylactone (A.,



1930, 1588) are *el.*-lactoid (*L*⋖⋗*M*) and blue salts are *el.*-furoid (*L*⋗⋗*M*). Absorption spectra support this view. R. S. C.

IV.—STEROLS AND STEROID SAPOGENINS.

Water-in-oil emulsifying agents. II. Synthesis of cholesteryl and cetyl esters. E. L. Cataline, L. Worrell, S. F. Jeffries, and S. A. Aronson (*J. Amer. Pharm. Assoc.*, 1944, **33**, 107—108; cf. Powers *et al.*, B., 1940, 402).—The following were prepared from the acid (0·02), alcohol (0·02 or 0·04), and *p*-C_6H_4Me·SO_3H (0·0015 mol.) in C_6H_6 (150 ml.) at 130—140° (bath) for 3 hr.: cholesteryl *n*-butyrate, m.p. 102° (clears at 110°), *n*-hexoate, m.p. 98—99°, laurate, m.p. 91—92°, myristate, m.p. 80° (86°), palmitate, m.p. 89—90°, stearate, m.p. 82—83°, and H succinate, m.p. 175—175·5°; dicholesteryl oxalate, m.p. 226—227°, succinate, m.p. 220° (240°), and adipate, m.p. 195° (222°); *cetyl laurate*, m.p. 40—41°, myristate, m.p. 47—48°, palmitate, m.p. 53—54°, stearate, m.p. 56—57°, and λ-hydroxystearate, m.p. 68—69°; dicetyl oxalate, m.p. 56·5—57·5°, succinate, m.p. 58·5—59°, and adipate, m.p. 56·5—57°. The use of these substances for emulsions is discussed. F. O. H.

Bromination of cholesteryl benzoate. H. Bretschncider, Z. Foldi, F. Galinovsky, and G. von Fodor (*Ber.*, 1941, **74**, [*B*], 1451—1455).—Cholesteryl benzoate (**I**) and Br in $CHCl_3$ at 1° give stereoisomeric dibromides (**II**), m.p. 138—140° (after sintering), 136·5—137·5

(vac.), $[\alpha]_D^{18}$ −40·31° in $CHCl_3$, and (**III**), m.p. 158—160° (decomp.), $[\alpha]_D$ +80° in $CHCl_3$ (cf. Obermüller, A., 1891, 298; Dorée *et al.*, A., 1916, i, 261; Petrow, A., 1937, II, 417). The structure of (**II**) is proved by its normal mol. wt. (cryoscopic in C_6H_6), behaviour as a single substance on chromatography (Al_2O_3), reduction to (**I**) by H_2–Pd–C in Et_2O, and by conversion into (**III**) by heating in EtOH. In boiling C_6H_6 or $CHCl_3$, (**II**) or (**III**) gives an equilibrium mixture containing 79—83% of (**III**) as judged by $[\alpha]$. The 5 : 5′-dibromo-3 : 3′-dibenzoyloxy-6 : 6′-dicholestanyl of Petrov (*loc. cit.*) is (**II**). R. S. C.

Steroids and sex hormones. XCIV. Introduction of a hydroxyl group in position 5 of the sterol skeleton by hydrogenation of 5 : 6- or 4 : 5-oxido-compounds. P. A. Plattner, T. Petrzilka, and W. Lang (*Helv. Chim. Acta*, 1944, **27**, 513—524).—Hydrogenation of cholesteryl acetate α-oxide (**I**) leads smoothly to the production of 5-OH-compounds, whereas a similar treatment of the β-compounds gives 6-OH-derivatives, whilst the oxido-O and that attached to $C_{(3)}$ are in part removed. Hydrogenation of 4 : 5- or 5 : 6-oxides in the steroid series gives a means of introducing OH at $C_{(5)}$. The course of the change appears to depend considerably on experimental conditions, the configuration of the oxide, and the presence of substituents at vicinal C atoms. (**I**) is hydrogenated homogeneously (PtO_2 in AcOH) to *5-hydroxy-3(β)-acetoxycholestane* (**II**), m.p. 185—185·5°, $[\alpha]_D$ +12·5°, +10·7° (*c* = 0·83, 0·423) in $CHCl_3$, which gives a very stable chromate with CrO_3 in AcOH, hydrolysed [as is (**II**)] to 3(β) : *5-dihydroxycholestane* (**III**), m.p. 224—225°, $[\alpha]_D$ +20·6°, +16·9° (*c* = 0·477, 0·860) in $CHCl_3$, converted by boiling Ac_2O (2 hr.) into (**II**) and by AcCl–$NPhMe_2$ in boiling $CHCl_3$ into the 3(β) : *5-diacetate*, m.p. 140—141°, $[\alpha]_D$ +31·8° (*c* = 1·220) in $CHCl_3$. (**III**) is oxidised by CrO_3 in 90% AcOH at room temp. to *5-hydroxy-3-ketocholestane*, m.p. 205—208°, $[\alpha]_D$ +40·0° in $CHCl_3$, dehydrated by boiling Ac_2O to Δ⁴-cholestenone. The product obtained by the action of per-acids on cholesteryl acetate is an additive compound (*A*), m.p. 114—115°, of (**I**) and cholesteryl acetate β-oxide (**IV**), m.p. 113—114°, $[\alpha]_D$ −1·0° (*c* = 1·004) in $CHCl_3$, separable into its components by chromatography over Al_2O_3. (*A*) is also obtained from cholestane-3 : 5 : 6-triol. (**IV**) is hydrolysed (boiling 0·5N-NaOH–MeOH) to *cholesterol β-oxide*, m.p. 132°, $[\alpha]_D$ +10·3° (*c* = 0·509) in $CHCl_3$, and is hydrogenated (PtO_2 in AcOH) to cholestane (**V**), m.p. 80—81°, cholestanyl 3(β)-acetate (**VI**), m.p. 109—110°, and 6-*hydroxy*-3(β)-*acetoxy*- (**VII**), m.p. 143—144°, $[\alpha]_D$ −6·6° in $CHCl_3$ [oxidised to 6-keto-3(β)-acetoxy-, m.p. 128—129°], acetylated (Ac_2O–C_5H_5N at room temp.) to 3(β) : 6-*diacetoxy*-, m.p. 137·5—138·5°, *-cholestane*. Hydrogenation (PtO_2 in AcOH) of (*A*) with subsequent chromatography leads to (**V**), (**VI**), and (**VII**) with a mixture probably of (**VI**) and (**II**). Absorption of H_2 by (*A*) is not observed in presence of PtO_2–EtOAc, PtO_2–EtOH, Raney Ni in EtOH or EtOH + a little conc. NaOH, Pd–$CaCO_3$ in EtOAc, or PtO_2 in EtOAc containing a little AcOH. 5 : 6-Oxidocholestane, m.p. 79·7—80·5°, $[\alpha]_D$ −55·9° in $CHCl_3$, is hydrogenated to (**V**) and a non-cryst. product, oxidised (CrO_3 in AcOH at room temp.), and then separated into cholestan-6-one, m.p. 98—99°, and *5-hydroxycholestane*, m.p. 109—110°, $[\alpha]_D$ +11·2°, +9·3° (*c* = 0·89, 0·92) in $CHCl_3$. 4 : 5-Oxidocholestane ["coprostene oxide"], m.p. 95—96°, $[\alpha]_D$ +80·3° in $CHCl_3$, is hydrogenated (PtO_2 in AcOH) to 5- and 4-, m.p. 187—187·5°, $[\alpha]_D$ +2·8° in $CHCl_3$, -hydroxycholestane. Cholesterol α-oxide has $[\alpha]_D^{17}$ −43·1° in C_6H_6 (cf. lit.). M.p. are corr. H. W.

Steroids and sex hormones. XCIII. Hydrogenation of the two oxides of *trans*-dehydroandrosterone acetate. L. Ruzicka and A. C. Muhr (*Helv. Chim. Acta*, 1944, **27**, 503—512).—*trans*-Dehydroandrosterone acetate is converted by *o*-$CO_2H{\cdot}C_6H_4{\cdot}CO_2H$ in CCl_4 into α-(**I**), m.p. 222—224°, $[\alpha]_D^{14}$ −12° in $CHCl_3$, $[\alpha]_D^{16}$ −12·4° in $COMe_2$, and β- (**II**), m.p. 186—187°, $[\alpha]_D^{15}$ +40·7° in $CHCl_3$, +47° in $COMe_2$, -5 : 6-oxido-3(β)-acetoxyandrostan-17-one. (**I**) is hydrogenated (PtO_2 in AcOH) to 5 : 17-*dihydroxy*-3(β)-*acetoxyandrostane* (**III**), m.p. 192—197°, oxidised (CrO_3 in AcOH) to *5-hydroxy*-3(β)-*acetoxyandrostan-17-one* (**IV**), m.p. 152·5—153·5° and 162·5—163·5° after resolidification, $[\alpha]_D^{13}$ +59·3° in $CHCl_3$, which is stable towards Ac_2O–C_5H_5N and BzCl–C_5H_5N in the cold and is hydrolysed (K_2CO_3 in aq. MeOH) to 3(β) : 5-*dihydroxyandrostan*-17-*one*, m.p. 281—282° (vac.; partial sublimation), $[\alpha]_D^{15}$ + 92·8° in MeOH; this is oxidised [$Al(OBu^t)_3$ in abs. $COMe_2$–dioxan] to Δ⁴-androstene-3 : 17-dione, m.p. 171—172·5°, $[\alpha]_D$ +190·5° in $CHCl_3$. Partial hydrogenation (PtO_2 in AcOH) of (**I**) gives unchanged material, and (**IV**) which is reduced to (**III**), whereas partial hydrogenation in EtOH affords α-5 : 6-*oxido*-17-*hydroxy*-3(β)-*acetoxyandrostane*, m.p. 146—147° and 152·5—153·5° after resolidification, $[\alpha]_D^{14}$ −66° in $CHCl_3$ [yielding α-5 : 6-*oxido*-3(β) : 17-*diacetoxyandrostane*, m.p. 165—166°, $[\alpha]_D^{14}$ −69·3°, hydrogenated to (**III**)]. Total hydrogenation (PtO_2 in AcOH or, more slowly, in EtOH) of (**II**) leads to 17(α)-hydroxyandrostane (**V**), m.p. 164—166°, $[\alpha]_D^0$ +13·1° in $CHCl_3$, oxidised to androstan-17-one (**VI**), m.p. 119·5—120·5°, $[\alpha]_D^1$ +87·8° in $CHCl_3$; partial hydrogenation (PtO_2 in AcOH) gives unchanged material, (**V**), (**VI**), and 6 : 17-*dihydroxy*-3(β)-*acetoxyandrostane*, m.p. 204—207°, oxidised (CrO_3 in AcOH) to 6 : 17-diketo-3(β)-acetoxyandrostane, m.p. 203—205°, $[\alpha]_D^{18}$ +39·2° in $CHCl_3$. H. W.

Steroid ketones.—See B., 1944, III, 119.

Steroids and sex hormones. XCV. Preparation of 2-keto-, 2(α)- and 2(β)-hydroxy-cholestane. L. Ruzicka, P. A. Plattner, and M. Furrer (*Helv. Chim. Acta*, 1944, **27**, 524—530).—3-Keto-2-cholestanylpyridinium bromide is converted by *p*-$NO{\cdot}C_6H_4{\cdot}NMe_2$ and N-NaOH in $CHCl_3$–EtOH at 20° into the corresponding *nitrone*, $C_{35}H_{54}O_2N_2$, m.p. 178—179° (decomp.), converted by 2N-HCl–Et_2O into form *A*, m.p. 135—137°, $[\alpha]_D$ +75° in $CHCl_3$ (cf. Stiller *et al.*, A., 1938, II, 193), of 2 : 3-diketocholestane; this is converted by Ac_2O–C_5H_5N at 100° into the *enol acetate* A, m.p. 138—139°, $[\alpha]_D$ +96° in $CHCl_3$, hydrolysed to homogeneous Δ³-2-ketocholesten-3-ol. This with *p*-$C_6H_4Me{\cdot}SO_2Cl$ in C_5H_5N at 20° gives the 3-*p*-*toluenesulphonate* (**I**), m.p. 161—162°, $[\alpha]_D$ +83° in $CHCl_3$, which is converted by NaI in anhyd. $COMe_2$ at 160° into Δ³:⁵-*cholestadien*-2-*one*, m.p. 121·5—122·5°, $[\alpha]_D$ −62° in $CHCl_3$ [hydrogenated (PtO_2 in AcOH) and then oxidised (CrO_3) to *cholestan*-2-*one* (**II**), m.p. 130·5—131·5°, $[\alpha]_D$ +49° in $CHCl_3$, also obtained by hydrogenation (Raney Ni in EtOH at 70°) and subsequent oxidation of (**I**)]. Oxidation of (**II**) by CrO_3 in 90% AcOH at 60° affords the dicarboxylic acid, $C_{27}H_{46}O_4$, m.p. 194—196° (Me_2 ester, m.p. 59—60°), obtained by Windaus *et al.* (A., 1915, i, 678) by oxidation of cholestanol. (**II**) is hydrogenated (PtO_2 in AcOH) to 2(β)(?)-*hydroxycholestane*, m.p. 154—155°, $[\alpha]_D$ +33° in $CHCl_3$, the configuration assigned to which is based on its precipitability with digitonin. With Na and EtOH (**II**) affords 2(α)(?)-*hydroxycholestane*, m.p. 178—180°, $[\alpha]_D$ +36° in $CHCl_3$ (no ppt. with digitonin). M.p. are corr. H. W.

Lumicœstrone. A. Butenandt, A. Wolff, and P. Karlson (*Ber.*, 1941, **74**, [*B*], 1308—1312).—Irradiating (ultra-violet) œstrone (**I**) in dioxan–N_2 gives *lumicœstrone* (**II**), m.p. 268—269°, $[\alpha]_D^{21}$ −43°, $[\alpha]_D^{5}$ −45·5° in dioxan [*acetate*, m.p. 89—90°; *Me ether* (**III**), m.p. 129—130°, $[\alpha]_D^{23}$ −28° in $CHCl_3$], which gives an *oxime*, m.p. 200—202°, and *semicarbazone* (**IV**), m.p. 273° (micro), only with difficulty. NaOEt–EtOH at 190—200° reduces (**IV**) to *deoxolumicœstrone*, m.p. 170—171°, which could not be obtained by irradiating deoxocœstrone. Pd-black at 260° converts (**I**) into *d-iso*equilenin (14-*epi*equilenin), m.p. 257—258°, $[\alpha]_D^{20}$ +152° in dioxan (cf. A., 1939, II, 76), but converts (**II**) into *l-iso*equilenin, m.p. 256—258°, $[\alpha]_D^{0}$ −151° in dioxan (*dl*-compound, m.p. 222—223°) (cf. A., 1940, II, 225). Na–$Pr^{\alpha}OH$ reduces (**III**) to *lumicœstradiol Me ether*, m.p. 137—138°, $[\alpha]_D^{20}$ +15·5° in $CHCl_3$. Since Pd-black isomerises $C_{(14)}$, irradiation of (**I**) probably isomerises $C_{(13)}$, so that (**II**) is 13-epicœstrone, but inversion at $C_{(8)}$ may also have occurred. R. S. C.

Conversion of Δ⁴-cholestene-3 : 6-dione into cholestan-3-ol-6-one by partial reduction. H. Bretschneider (*Ber.*, 1941, **74**, [*B*], 1361—1363).—1 mol. of H_2 is rapidly and a second mol. more slowly absorbed by Δ⁴-cholestene-3 : 6-dione. After 2 mols. have been absorbed in presence of Raney Ni in EtOH, cholestan-3-ol-6-one is obtained; partial hydrogenation in presence of 20% Pd–C in AcOH gives cholestane-3 : 6-dione. R. S. C.

Oxidation of cholestenone by oxygen. Formation of progesterone. H. Bretschneider (*Ber.*, 1941, **74**, [*B*], 1360—1361).—O_2 is blown into cholestenone (4 pts.) and V_2O_5 (1 pt.) at 170°; alkali-sol. products are removed. Shaking the Et_2O-solution of the residue repeatedly with conc. HCl removes substances, whence chromatography yields progesterone. R. S. C.

Diginin. III. Degradation of diginigenin to a hydrocarbon diginane. C. W. Shoppee (*Helv. Chim. Acta*, 1944, **27**, 246—260; cf. A., 1943, II, 151).—Direct oxidation of diginigenin (**I**) gives mixtures of neutral and acid products from which individuals cannot be isolated. Treatment of (**I**) or its semicarbazone with N_2H_4,H_2O–NaOEt in EtOH at 180° leads to a mixture (**II**) of substances from which *deoxodiginigenin* (**III**), $C_{31}H_{50}O_3$, m.p. 163—164° (*hydrate*, m.p. 86°), $[\alpha]_D^{15}$ −71·5°±4° in $COMe_2$, is most readily isolated. The presence of a *sec.* OH in (**III**) is established by the isolation of an *acetate*, m.p. 61—62°, hydrolysed to (**III**), but the functions of the remaining, non-reactive O atoms are not elucidated. (**III**) does not reduce Ag_2O–NH_3 at 20° and gives negative Raudnitz–Puluj, Legal, and Zimmermann tests. Under energetic conditions it does not afford an oxime. (**III**) is readily hydrogenated (PtO_2 in AcOH) to *dihydrodeoxodiginigenin* (**IV**), m.p. 190—191°, $[\alpha]_D^{16}$ +7·9°±2° in $COMe_2$ (*acetate*, an oil), which does not give a yellow colour with $C(NO_2)_4$. N_2H_4 and alkali yield resinous products or unchanged material from (**IV**). CrO_3 smoothly oxidises (**IV**) to *dihydrodehydrodeoxodiginigenin* (**V**), m.p. 178—179°, $[\alpha]_D^{16}$ +21·5°± 2·5° in $COMe_2$ (*oxime*, m.p. 159—160), reduced (Wolff–Kishner) to *dihydrodeoxydeoxodiginigenin*, m.p. 113—115°, becomes opaque at 60—70°, $[\alpha]_D^{3}$ +10°±3° in $COMe_2$, which retains only the two non-reactive O of (**I**) and does not give a cryst. product with Ac_2O at 200°. (**V**) is reduced (Clemmensen) and subsequently hydrogenated (PtO_2 in AcOH) to a liquid *substance*, $C_{21}H_{32(34)}O$, which does not give a yellow colour with $C(NO_2)_4$ and has not been further studied since isomerisations may have occurred in its production. Chromatographic purification of (**II**) leads also to Δ¹-*dihydroxyketodiginene* (**VI**), $C_{21}H_{32}O_3$, m.p. 147°, $[\alpha]_D^{17}$ −24°±2° in $COMe_2$, which gives a non-cryst. *diacetate*, hydrolysed to (**VI**). CO does not appear present in (**VI**), which gives negative Raudnitz–Puluj, Legal, and

Zimmermann tests. (**VI**) gives a marked yellow colour with $C(NO_2)_4$ and is readily hydrogenated to the saturated *dihydroxyketodiginane* (**VII**), m.p. 195—196°, $[\alpha]_D^{17}$ −20°±3° in $COMe_2$, which yields a non-cryst. *diacetate*, hydrolysed to (**VII**). CrO_3 oxidises (**VII**) to (impure) triketodiginane, which gives a 2 : 4-*dinitrophenylhydrazone*, m.p. (indef.) 120°, and a *dioxime*, softens 180—200° (decomp.), and probably contains the non-reactive :CO of (**I**). The residue left after (**II**) has been freed as completely as possible from (**III**) and (**VI**) gives after hydrogenation (PtO_2 in AcOH) *dihydroxydiginane* (**VIII**), plates which become opaque at ~105°, are converted without melting into needles at 140—142° and then have m.p. 153—154°, or, after sublimation, m.p. 155—156°, $[\alpha]_D^2$ +25·4°±2° in $CHCl_3$; the non-cryst. *diacetate* is hydrolysed to (**VIII**). CrO_3 oxidises (**VIII**) smoothly to *diketodiginane*, m.p. 140—141°, $[\alpha]_D^{13}$ +39·5°±2° in $COMe_2$ (*bis*-2 : 4-*dinitrophenylhydrazone*, m.p. 185°), reduced (Wolff–Kishner) to *diginane*, $C_{21}H_{36}$, m.p. 75—77°, $[\alpha]_D^0$ +24°±4°, $[\alpha]_{5461}^{20}$ +27·5°±4° in $CHCl_3$. M.p. are corr. (block); limit of error ~±2°.

H. W.

Diginin and diginigenin. IV. C. W. Shoppee (*Helv. Chim. Acta*, 1944, **27**, 426—435; cf. preceding abstract).—The experimental results do not justify the consideration of diginigenin (**I**) as a steroid but they can all be brought into harmony with the structure (*A*) (R = H) for (**I**) and (R = $C_7H_{13}O_3$) for diginin. Such a formulation expresses the possible biogenetic relationship with the steroid digitalis saponins and sapogenins. The observation that mild oxidation of (**I**) and its monoacetate does not yield well-defined acids indicates that the CO group is present as ketone in the group ·C·CO·CH_2·O·C·. The few substances described in the literature with this arrangement show, like (**I**), strong reducing action and positive reactions with 1 : 4-$C_{10}H_6(OH)_2$ and according to Legal and Zimmermann. The latter reactions are characteristic of activated CH_2 and are not shown by derivatives of (**I**) obtained by hydrogenation or reduction (Wolff–Kishner). The presence of CH_2·CO· in (**I**) is confirmed by the isolation of piperonylidenediginigenin (*monohydrate*, m.p. 128—131°). Diginigenin monoacetate is hydrogenated (PtO_2 in AcOH at 17°) to tetrahydrodiginigenin monoacetate (**II**), prisms, m.p. 174°, or *needles*, m.p. 156°, slowly converted by Ac_2O in C_5H_5N into the *diacetate*, m.p. 120—121°, $[\alpha]_D$ +17°±2° in $COMe_2$. (**II**) is oxidised by CrO_3 in AcOH at 15° to the amorphous dihydrodiginigenin monoacetate (*semicarbazone*, m.p. 226°), which has strong reducing power and gives the three colour changes. Energetic acetylation converts it into a non-cryst., unsaturated compound, apparently an enol diacetate, since it is transformed by ozonisation followed by treatment with hot H_2O into a cryst. acid, $C_{23}H_{32}O_7$, m.p. 302—304°, the *Me* ester, m.p. 203—204°, of which does not react with 2 : 4-dinitrophenylhydrazine sulphate and reduces Ag_2O–NH_3 when heated but not appreciably at 20°. Hexahydrodiginigenin diacetate (**III**) is quantitatively hydrolysed to the parent compound, which is converted by short treatment with boiling Ac_2O into the *monoacetate*, m.p. 83°, and with Ac_2O and C_5H_5N at 100° into a non-cryst. diacetate possibly identical with (**III**). The reducing power and colour reactions of many derivatives of (**I**) are described. ω-Methoxyacetophenone, b.p. 122°/15 mm., has been obtained from CH_2Ac·OMe and MgPhBr. M.p. are corr. (block); limits of error ±2°.

H. W.

V.—TERPENES AND TRITERPENOID SAPOGENINS.

Factors determining the course and mechanism of Grignard reactions. XII.—See A., 1944, II, 215.

Triterpene resinols and related acids. XVI. Preliminary examination of a major oxidation product of the β-amyrin group. N. Mower, J. Green, and F. S. Spring (*J.C.S.*, 1944, 256—260).—Oxidation of either β-amyrenonyl acetate, $C_{32}H_{50}O_3$, or β-amyradienonyl acetate (**I**), $C_{32}H_{48}O_3$, with SeO_2 gives an acetate (**II**), $C_{32}H_{46}O_5$ ("O_5-acetate"), m.p. 252—253°, $[\alpha]_D^{23}$ +35° (*c* = 2·1). Similar oxidation of corresponding benzoates gives the *benzoate*, $C_{37}H_{48}O_5$, m.p. 262—263°, $[\alpha]_D^2$ +42° (*c* = 2·0). Oxidation (H_2CrO_4) of β-amyradienyl-II acetate yields (**II**) with some (**I**). Treatment of (**II**) with KOH affords, in high yield, a yellow amorphous product, acetylation of which does not regenerate (**II**) but a *diacetate*, $C_{\infty}H_{\infty}O_5$ (?), m.p. 249—251°, $[\alpha]_D^{22}$ +149° (*c* = 0·7). Hydrolysis (MeOH–HCl) of (**II**) gives the parent *alcohol*, $C_{30}H_{44}O_4$, m.p. 280·5—281·5°, reacetylated to (**II**). It is shown that (**II**) does not contain either a OH or reactive CO and is resistant to catalytic hydrogenation. This new type of oxidation product is found to be characteristic of the β-amyrin group; SeO_2 treatment of either Me ketoacetyloleanolate or H_2CrO_4 oxidation of Me acetyldehydro-oleanolate affords an *acetate*, $C_{33}H_{46}O_7$, m.p. 253—254°, $[\alpha]_D^{15}$ +15·9° in C_5H_5N (*alcohol*, $C_{31}H_{44}O_6$, m.p. 255—256°, $[\alpha]_D^6$ −3·55° in C_5H_5N), which is an exact analogue of (**II**).

F. R. S.

Hydration of camphene to *iso*borneol. L. M. Pesin, E. T. Beljanina, and V. A. Pavlovskaja (*J. Appl. Chem. Russ.*, 1943, **16**, 129—133).—Hydration of camphene (1 part), m.p. 42°, by "Kontakt" (petroleum sulphonic acids) (3 parts) at 50° (12 hr.) yielded up to 90% of crude cryst. *iso*borneol, m.p. 186°. The best results are obtained by freeing the "Kontakt" from mineral oil but not from H_2SO_4.

V. B.

Camphyl compounds.—See B., 1944, II, 198.

4-Camphorylthiosemicarbazide and 4-camphorylsemicarbazide. J. A. McRae and W. H. Stevens (*Canad. J. Res.*, 1944, **22**, B, 45—52).—Camphorylthiocarbimide (**I**) (from camphoryldithiocarbamic acid and BzCl–C_5H_5N, or HNO_2) with N_2H_4,H_2O in EtOH at 0° gives a little dicamphorylthiocarbamide, m.p. 176°, and (80% yield) 4-*camphorylthiosemicarbazide* (**II**), m.p. 168° (corr.), $[\alpha]_D$ +17·34° in $CHCl_3$. (**II**) with dil. HCl or NaOH at room temp. yields the *anhydride*, m.p. 239°, $[\alpha]_D$ +281·5° in $CHCl_3$, which, by conversion into its Ag derivative and treatment with MeI, gives the *monomethylanhydride*, m.p. 107°, $[\alpha]_D$ −57·4°. (**II**) with BzCl in C_5H_5N yields the 1-*benzoate*, m.p. 225°, and with PhNCO N-*anilinoformyl*-N′-*camphorylaminothioformylhydrazine*, m.p. 139—143° (decomp.). (**II**) with the corresponding aldehyde in EtOH gives *benzylidene*-, m.p. 215—216°; $[\alpha]_D$ +68·6° in $CHCl_3$, p-, m.p. 234°, $[\alpha]_D$ +105·2° in $CHCl_3$, and m-*nitrobenzylidene*-, m.p. 140°, *anisylidene*-, m.p. 148—149°, $[\alpha]_D$ +83·8° in $CHCl_3$, and 3 : 4-*diethoxybenzylidene*-, m.p. 111—113°, $[\alpha]_D$ +34·6° in $CHCl_3$, *-camphorylthiosemicarbazone*, but many aldehydes and ketones do not give cryst. products. The possible use of (**II**) as resolving agent for *dl*-carbonyl compounds is thus limited. (**I**) with $ArNH{\cdot}NH_2$ in hot EtOH gives the corresponding *-4-camphorylthiosemicarbazides*: 1-o-, m.p. 171°, $[\alpha]_D$ +34·6° in $CHCl_3$, and 1-p-*tolyl*-, m.p. 226°, $[\alpha]_D$ +231·6° in $CHCl_3$, 1-m-*nitrophenyl*-, m.p. 204° (decomp.), $[\alpha]_D$ +313·4° in $CHCl_3$, (decomp. on keeping), 1-p-*bromophenyl*-, m.p. 227° (decomp.), $[\alpha]_D$ +15·2° in EtOH, 1-(2′ : 4′-*dinitrophenyl*)-, m.p. 218°, 1-β-*naphthyl*-, m.p. 191°, $[\alpha]_D$ +51·1° in $CHCl_3$, in all of which the 1-position assigned to the aryl group is tentative. (**I**) with $NPh_2{\cdot}NH_2$ gives 1 : 1-*diphenyl*-4-*camphorylthiosemicarbazide*, m.p. 223°, $[\alpha]_D$ −26·9° in $CHCl_3$. Camphorylcarbimide with N_2H_4,H_2O yields 4-*camphorylsemicarbazide* (**III**), m.p. 215°, $[\alpha]_D$ −26·3° in EtOH. With aq. HCl (**III**) gives the *anhydride*, sublimes 325°, $[\alpha]_D$ +115·4° in EtOH, and m-, m.p. 178°, and p-*nitrobenzylidenesemicarbazones*, m.p. 223°, and other non-cryst. semicarbazones.

D. G.

VI.—HETEROCYCLIC.

Action of sodium cyanide on methyl γ-bromo-αα-dimethylacetoacetate. C. F. Koelsch (*J. Amer. Chem. Soc.*, 1944, **66**, 306—307).—Contrary to Lawrence (*J.C.S.*, 1899, **75**, 417) and Conrad *et al.* (A., 1899, i, 258; 1900, i, 475), $CH_2Br{\cdot}CO{\cdot}CMe_2{\cdot}CO_2Me$ and NaCN give *Me* β-*cyano*-β-*epoxy*-αα-*dimethyl*-n-*butyrate* (not $CN{\cdot}CH_2{\cdot}CO{\cdot}CMe_2{\cdot}CO_2Me$), since hydrolysis yields 4-*hydroxy*-2-*keto*-3 : 3-*dimethyltetrahydrofuran*-4-*carboxylic acid* (**I**) (not the 5-carboxylic acid), m.p. 213—217° (Me ester, m.p. 104—105°), the structure of which is proved by synthesis. $OAc{\cdot}CH_2{\cdot}CO{\cdot}CMe_2{\cdot}CO_2Me$ (stable when heated with K_2CO_3 or kept; cf. lit.) and boiling HCl–EtOH give 2 : 4-diketo-3 : 3-dimethyltetrahydrofuran (86%), b.p. 200—210°/740 mm., 103—107°/6 mm., which with aq. HCl–NaCN gives an oily cyanohydrin, hydrolysed to (**I**) by boiling 20% HCl.

R. S. C.

Furfurylamines.—See B., 1944, II, 198.

5-Hydroxy- and -methoxy-flavylium salts. L. R. Row and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1944, **19**, A, 141—145).—Condensation of γ-resorcylaldehyde and its Me ether (improved preps.) in EtOAc–HCl with the appropriate substituted COPhMe gives 3 : 5 : 4′-*trihydroxy*-, m.p. >300°, 3 : 4′-*dihydroxy*-5-*methoxy*-, m.p. 258—260°, 3 : 5 : 3′ : 4′-*tetrahydroxy*-, m.p. >300°, and 3 : 5 : 3′ : 4′ : 5′-*pentahydroxy*-*flavylium chloride*, m.p. >300°. These substances exhibit negligible fluorescence even in conc. H_2SO_4. The structural factors which affect fluorescence in flavylium salts are discussed; comparison is made with coumarins.

F. R. S.

Benzopyrylium salts. IV. Nitration of 2 : 3-diphenylbenzopyrylium perchlorate. R. L. Shriner and R. B. Moffett (*J. Amer. Chem. Soc.*, 1944, **66**, 301—302; cf. A., 1942, II, 109).—The position of NO_2 entering 2-phenylflavylium perchlorate (**I**) is governed by electronic considerations on the assumption that the salt has carbenium structure. In fuming HNO_3 at 0°, (**I**) gives crude 3-p-*nitrophenylflavylium perchlorate* (**II**) (53·5%), m.p. ~217° (decomp.), and thence the ferrichloride (**III**), m.p. 136—137°. Pure (**II**) (93·5%), m.p. 235—237° (decomp.), and thence (**III**), m.p. 137—138°, is obtained from *p*-$NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}COCl$, *o*-$OH{\cdot}C_6H_4{\cdot}CHO$ (**IV**), HCl (gas), and 72% $HClO_4$ in AcOH. In H_2SO_4–HNO_3 at <0° and then 45°, (**I**) or (**II**) gives 3′-*nitro*-3-p-*nitrophenylpyrylium perchlorate* (**V**) (>90%), m.p. 258—258·5° (decomp.), also obtained from (**IV**), *p*-$NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CO{\cdot}C_6H_4{\cdot}NO_2$-*m*, HCl, and 72% $HClO_4$–AcOH. In boiling MeOH, (**V**) gives 2-*methoxy*-2-m-*nitrophenyl*-3-p-*nitrophenyl*-Δ^3-*chromene*, m.p. 178—179° (177·5—178·5°).

R. S. C.

Santonin series. I. Two new desmotroposantonins and two new desmotroposantonous acids. M. Huang, C. P. Lo, and L. J. Chu (*J. Chinese Chem. Soc.*, 1943, **10**, 126—135).—Santonin (**I**) and

Ac_2O (+H_2SO_4) at 100° (bath) or at room temp. (2 weeks) give *l*-α-desmotroposantonin acetate, m.p. 156—157°, hydrolysed by boiling 10% aq. NaOH to *l*-α-desmotroposantonin (**II**), m.p. 194—195°. *d*-β-Desmotroposantonin (**III**), m.p. 260—261°, $[\alpha]_D^{21}$ +106·2° in EtOAc (acetate, m.p. 154—155°), is obtained from (**I**) or (**II**) and boiling aq. H_2SO_4, and *l*-β-*desmotroposantonin* (**IV**), m.p. 260—261°, $[\alpha]_D^{21}$ −106·2° in EtOAc (acetate, m.p. 156—157°), is similarly formed from the *d*-α-form, m.p. 196—196°. (**IV**) is probably identical with the *l*-desmotroposantonin, m.p. 253°, described by Clemo (A., 1934, 1225), and is converted by aq. KOH at 210° (oil-bath) into (**II**). Equal amounts of (**III**) and (**IV**) in boiling EtOAc, on cooling, yield the dl-β-*compound* (**V**), m.p. 231—232° (Ac_2O–NaOAc gives the acetate, m.p. 182—183°, also obtained from the *d*-β- + *l*-β-acetates), converted by aq. KOH at 210° into dl-α-*desmotroposantonin*, m.p. 200—201°, which is formed also from the *d*- + *l*-α-forms, and is reconvertible into (**V**) by boiling aq. H_2SO_4. (**IV**) and Zn dust in boiling aq. AcOH yield d-β-*desmotroposantonous acid*, m.p. 175—176°; the *d*-α-analogue has m.p. 177—178°. dl-β-*Desmotroposantonous acid*, m.p. 180—181°, is obtained from the *d*- + *l*-β-forms or by reducing (**V**). The above nomenclature replaces the system of *iso*desmotropo- by *d*-α-desmotropo-, the *l*- by *l*-α-, and *dl*- by *dl*-α-; the lower-melting series is designated by α; desmotroposantonin is referred to as the *d*-β-form. The isolation of (**IV**) allows the transformation of any known active stereoisomeride of desmotroposantonin into others by acid or alkali treatment, as above. A. T. P.

Dioxan diphosphate. E. Baer (*J. Amer. Chem. Soc.*, 1944, **66**, 303).—Dioxan (**I**) (vapour or liquid) and H_3PO_4 give (exothermally if liquids) *dioxan* 1 : 4-*diphosphate*, sinters 78°, m.p. 83—87° (sealed tube), sol. in many org. solvents, dissociating in H_2O, stable at room temp. or, for a short time, at 150°, giving at 175° (**I**) and a little MeCHO, and with Na_2HPO_4 (2·2 mols.), K_3PO_4, or Na_3PO_4 (1·1 mol.) at 120—130° yielding (**I**) quantitatively. R. S. C.

Aldol condensation. III. Aldol–aldehyde addition products and their derivatives. R. H. Saunders and M. J. Murray (*J. Amer. Chem. Soc.*, 1944, **66**, 206—208).—Aldolisation of CHRR′·CHO leads to 1 : 3-dioxans (cf. A., 1944, II, 4), which with Ac_2O–C_5H_5N at room temp. yield 6-*acetoxy*-2 : 4-*dimethyl*-, b.p. 85·5°/10 mm., -5-*methyl*-2 : 4-*diethyl*-, b.p. 100°/7 mm., -5-ethyl-2 : 4-di-*n*-propyl-, b.p. 114°/3 mm., and -5 : 5-*dimethyl*-2 : 4-*diisopropyl*- (**I**), b.p. 93·5°/2 mm., -1 : 3-*dioxan*. d_4^{25}, $[M]_D$, and Raman spectra are recorded for these products and for 6-hydroxy-2 : 4-dimethyl-, -5-ethyl-2 : 4-di-*n*-propyl-, and -5-methyl-2 : 4-diethyl-1 : 3-dioxan, b.p. 91·5°/7 mm. The strongest line (at 834 cm.$^{-1}$) is due to the symmetrical breathing of the ring and a line at 1750 cm.$^{-1}$ to the ester-CO of the OAc. Compounds containing a neopentyl group show a strong line between 750 and 800 cm.$^{-1}$ Anhyd. 1% HCl–MeOH at room temp. converts (**I**) into 6-*methoxy*-5 : 5-*dimethyl*-2 : 4-*diisopropyl*-1 : 3-*dioxan*, b.p. 110°/20 mm. Further aldolisation of OH·CHPr$^{\beta}$·CMe$_2$·CHO being impossible, dissociation into Pr$^{\beta}$CHO occurs, which then yields 6-hydroxy-5 : 5-dimethyl-2 : 4-di*iso*propyl-1 : 3-dioxan and "paraldol" (the derived dimeric aldol), m.p. ~105—107°. R. S. C.

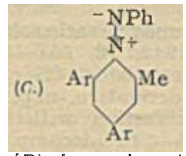
Alkyl exchange of carboxylic esters.—See A., 1944, II, 220.

Compounds of copper sulphate with pyridine. T. L. Chang and P. F. Hu (*J. Chinese Chem. Soc.*, 1943, **10**, 113—115).—$CuSO_4,5H_2O$ in aq. C_5H_5N and hot C_5H_5N–95% EtOH, on cooling, give *Cu*^{II} *sulphate tetrapyridine monohydrate* (**I**), $CuSO_4,4C_5H_5N,H_2O$. The use of relatively more EtOH affords *complexes*, $CuSO_4,3C_5H_5N,3H_2O$ (**II**) and $CuSO_4,2C_5H_5N,2H_2O$ (**III**); excess of 95% EtOH converts (**I**) or (**II**) into (**III**), and all the complexes lose C_5H_5N in air. A. T. P.

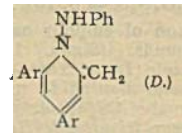
Pyridine acids.—See B., 1944, II, 198.

Condensation of 2- and 4-methylpyridine derivatives with cinnamaldehyde. E. Spath, G. Kubiczek, and E. Dubensky (*Ber.*, 1941, **74**, [*B*], 873—879).—In absence of $ZnCl_2$ (cf. Proske, A., 1909, i, 413) this condensation at 150—160° sometimes gives partly the butenol as well as the butadiene. 2-Methylpyridine and CHPh:CH·CHO (**I**) give α-*phenyl*-δ-2-*pyridyl*-Δ$^{\alpha}$-*buten*-γ-*ol* (**II**), m.p. 148°, and -Δ$^{\alpha\gamma}$-*butadiene*, m.p. 123—124° (*picrate*, m.p. 222°), hydrogenated (Pd-black; AcOH) to δ-phenyl-α-2-pyridyl-*n*-butan-β-ol, m.p. 36·5—37° (*picrate*, m.p. 107—109°), and -*n*-butane (*picrate*, m.p. 113—114°), respectively. 4-Methylpyridine and (**I**) give α-*phenyl*-δ-4-*pyridyl*-Δ$^{\alpha}$-*buten*-β-*ol*, m.p. 115—116°, and only traces of α-phenyl-δ-4-pyridylbutadiene, m.p. 157·5—159° [the sole product (m.p. 161—162°) in presence of Ac_2O at 170°]; hydrogenation (Pd-black; MeOH) then gives δ-phenyl-α-4-pyridyl-*n*-butan-β-ol (*picrate*, m.p. 109—110°). 2 : 6-Dimethylpyridine and (**I**) give α-phenyl-δ-6-methyl-2-pyridyl-Δ$^{\alpha}$-buten-γ-ol (*picrate*, m.p. 162°) and -Δ$^{\alpha\gamma}$-butadiene, m.p. 110—111° [*picrate*, m.p. 229° (decomp.)], hydrogenated to δ-phenyl-α-6-methyl-2-pyridyl-*n*-butan-β-ol (*picrate*, m.p. 117—118°) and α-phenyl-δ-6-methyl-2-pyridyl-*n*-butane (*picrate*, m.p. 87—88°); both condensation products are oxidised to BzOH and 6-methylpyridine-2-carboxylic acid, m.p. 128—129°. 2-Methylquinoline and (**I**) give only α-phenyl-δ-2-quinolylbutadiene, m.p. 119° [picrate, m.p. 244° (decomp.)], reduced as above to α-phenyl-δ-2-quinolyl-*n*-butane, an oil (*picrate*, m.p. 123—124°). Pd-black at 150° converts (**II**) into α-*phenyl*-δ-2-*pyridyl*-Δ$^{\alpha}$-*buten*-γ-*one*, m.p. 132—133° (*picrate*, m.p. 110—111°). R. S. C.

1-Arylaminopyridines. III. Influence of substituents [on the] constitution of anhydro-bases. W. Schneider and W. Riedel (*Ber.*, 1941, **74**, [*B*], 1252—1278).—Treating COArMe with H_2SO_4,H_2O and Ac_2O, first cold and then at 50—80°, gives 2 : 4-diaryl-6-methylpyrylium salts, which with NHAr′·NH_2 in hot C_6H_6 give 1-arylamino-2 : 4-diaryl-6-methylpyridinium salts (*A*). Heating (*A*) with alcoholic alkali gives highly coloured anhydro-bases which change to brown to red 2 : 4-diaryl-6-*o*-aminobenzylpyridines (*B*). The structure of (*B*) is shown by conversion of (*B*; aryl = Ph) into the *o*-NHBz-derivative, the *o*-NBz·NO-compound from which in boiling C_6H_6 gives an indazole derivative. The time taken for the anhydro-base to pass into (*B*) under standard conditions varies from 1·3 to 320 min., according to the substituents present in Ar and Ar′. It is assumed that the anhydro-bases exist as coloured (*C*) in equilibrium with (*D*) (by way of H-bridged ring intermediates) and that



(*C.*)



(*D.*)

only (*D*) isomerises to (*B*). The electronic nature of the substituents is shown to account semi-quantitatively for the variations in the time required for the change (*D*) → (*B*). The colour of the anhydro-base solutions accords approx. with the relative amounts of (*C*) believed to be present. The following are described. 2 : 4-*Di*-p-., m.p. 228° (corresponding sulphoacetate, m.p. 195°), and -m-*tolyl*-, m.p. 209°, 2 : 4-*di*-p-, m.p. 254° (decomp.), and -*m*-bromophenyl-, m.p. 182°, and 2 : 4-*di*-p-, m.p. 225°, and -*m*-chlorophenyl-, m.p. 189°, -6-*methylpyrylium iodide*. 2 : 4-Di-*p*-tolyl-6-ethylpyrylium sulphopropionate, m.p. 195° (decomp.), and iodide, m.p. 232·5°. 1-Anilino-2 : 4-di-*p*-anisyl-, m.p. 155°, -*p*-, m.p. 166°, and -*m*-tolyl-, m.p. 190·5°, -*p*-, m.p. 184·5°, and -m-*bromophenyl*-, m.p. 196·5°, -*p*-, m.p. 150·5°, and -m-*chlorophenyl*-, m.p. 181°, -6-*methylpyridinium iodide*. 1-*p*-Toluidino-2 : 4-di-*p*-anisyl-, m.p. ~134°, -p-, m.p. 172°, and -*m*-tolyl-, m.p. 154·5°, -*p*-bromophenyl-, m.p. 151°, -p-, m.p. 131°, and -*m*-chlorophenyl-, m.p. 153·5°, -6-*m*-ethylpyridinium iodide. 1-*p*-Bromoanilino-2 : 4-di-*p*-anisyl-, m.p. 152°, -*p*-tolyl-, m.p. 192° (decomp.), and -p-*bromophenyl*-, m.p. 180°, -6-*methylpyridinium iodide*. 1-*m*-Toluidino-2 : 4-di-*p*-tolyl-, m.p. 164°, and -2 : 4-di-*p*-chlorophenyl-, m.p. 179°, -pyridinium iodide. 2 : 4-Di-*p*-anisyl-, m.p. 137°, -*p*-, m.p. 126°, and -*m*-tolyl-, m.p. 131°, -p-, m.p. 164°, and -*m*-bromophenyl-, m.p. 139·5°, -*p*-, m.p. 150°, and -*m*-chlorophenyl-, m.p. 134°, -6-*o*-aminobenzylpyridine. 2 : 4-Di-*p*-anisyl-, m.p. 134°, -p-, m.p. 152°, and -*m*-tolyl-, m.p. 140°, -*p*-bromophenyl-, m.p. 165°, -*p*-, m.p. 148°, and -*m*-chlorophenyl-, m.p. 129°, -6-2′-amino-4′-methylbenzylmethylpyridine. 2 : 4-Di-*p*-anisyl-, m.p. 158·5°, -*p*-tolyl-, m.p. 162°, and -*p*-bromophenyl-, m.p. 156°, -6-2′-amino-4′-bromobenzylpyridine. 2 : 4-Di-*p*-tolyl-, m.p. 122°, and -*p*-chlorophenyl-6-2′-amino-3′- or -5′-methylbenzylpyridine, m.p. 160°. 1-Anilino-, 1-*p*-toluidino-, m.p. 145°, and 1-*p*-bromoanilino-2 : 4-diphenyl-6-ethylpyridinium iodide with alkali give blue anhydro-bases which very rapidly yield (?) 2 : 4-diphenyl-6-α-*o*-aminophenylethylpyridine etc. R. S. C.

New case of opening of the isatin ring. G. Jacini (*Gazzetta*, 1942, **72**, 510—514).—Isatin-3-imide with aq. NH_3–H_2O_2 gives o-*carboxylamidophenylcarbamide* (**I**) (picrate, m.p. 340°), which when heated decomposes to give 2 : 4-dihydroxyquinazoline (**II**). (**I**) is also obtained from *o*-NH_2·C_6H_4·CO·NH_2 (**III**) and KCNO in AcOH, or from (**II**) and EtOH–NH_3 at 100°. Isatin and aq. NH_3–H_2O_2 give *o*-NH_2·C_6H_4·CO_2H. Biuret and (**III**) at >145° give *dianthranylbiuret*, m.p. 315°, easily hydrolysed to (**II**). E. W. W.

Carbon-alkylation with quaternary ammonium salts. Synthesis of compounds containing the β-indolemethylene group. H. R. Snyder, C. W. Smith, and J. M. Stewart (*J. Amer. Chem. Soc.*, 1944, **66**, 200—204).—CH_2Ar·NR_2Hal reacts with CHXNa·CO_2R (X = CN, Ac, or CO_2Et) to give CH_2Ar·CHX·CO_2R, the yield depending largely on the conditions. CH_2Ar·NR_2 does not react unless X = CO_2Et, in which case the yield is poor. CH_2Ph·$NPhMe_2Cl$ (**I**) with CHNaAc·CO_2Et (**II**) in boiling EtOH gives 60% of CH_2Ph·CHAc·CO_2Et (2 : 4-*dinitrophenylhydrazone*, m.p. 71·5°), and with CHNa$(CO_2Et)_2$ (**III**) thus gives 37·6% of CH_2Ph·$CH(CO_2Et)_2$ (**IV**). With (**III**) in EtOH, 32, 36, 22, 36, 20, and 26% of (**IV**) are obtained from (**I**) at 115° or 130°, benzylmethylpiperidinium iodide (**V**) at 120° or 135°, or benzylmethylpiperidinium chloride at 135° or 130°, respectively, with notable amounts of $(CH_2Ph)_2C(CO_2Et)_2$ (identified by hydrolysis and decarboxylation), but $NPhMe_2$ does not react at 130°. CH_2Ph·$NPhMe_2$·OEt and (**III**) at 150° and then 110° give 51·3% of (**IV**). In absence of solvent at 110° and then 140° (**III**) and (**I**) give 79%, (**V**) and (**III**) in Bu_2O give 62·5%, and CH_2Ph·NMe_3Br and (**III**) in Bu_2O give 77% of (**IV**). 3-Dimethylaminomethylindole (**VI**) (prep. improved), m.p. 127—128°, and MeI–EtOH at room temp. and then 0° give the methiodide (**VII**),

which with (III) in Bu_2O at 110° and then 145° gives 85% of *Et α-carbethoxy-β-3-indolylpropionate* (85%), m.p. 62°, whence boiling 30% aq. NaOH yields the *dicarboxylic acid* (VIII), m.p. 178° (decomp.) (*diamide*, m.p. 206°), decarboxylated at 180—190° to β-3-indolylpropionic acid (IX), m.p. 132—133°. CN·CHNa·CO_2Et and (VII) give similarly an oil (87%) and thence by hydrolysis (IX). $K_2Ag(CN)_3$ and (VII) in boiling H_2O give an oil, hydrolysed by boiling 20% aq. KOH to 3-indolylacetic acid (46%; 11·4% by KCN), m.p. 164·5—165·5°. (III) and (VI) at 120—150° give, after hydrolysis, 41% of (VIII). R. S. C.

Pyridines and quinolines.—See B., 1944, II, 130.

Doebner reaction. IV. R. Ciusa (*Gazzetta*, 1942, **72**, 567—570).—*p*-NH_2·C_6H_4·SO_2·NH_2 with $AcCO_2H$ and PhCHO in EtOH gives 4-p*''-sulphamylanilo-5-keto-2-phenyl*-1-p*'-sulphamylphenylpyrrolidine*, m.p. 260—263°, and a solution which with Na_2CO_3 gives 6-*sulphamyl*-2-*phenylquinoline*-3-*carboxylic acid* [*Na* salt (+$2H_2O$)]. Using *p*-NH_2·C_6H_4·SO_2·NH·C_5H_4N, the product is a *cinchonic acid*, $C_{22}H_{15}O_4N_2S$, m.p. 157°. E. W. W.

Action of sulphur on heterocyclic compounds: carbazole thio-compounds. (Signa.) L. Raffa (*Gazzetta*, 1942, **72**, 557—563).—Carbazole (I) and S at ~240° give a product from which CS_2 extracts *dicarbazyl disulphide*, m.p. 218—221° (*Bz_2* derivative, m.p. 160—170°); the CS_2-insol. portion yields on extraction with $COMe_2$ *dicarbazyl trisulphide* [*Bz_2* derivative, m.p. 205—210° (decomp.)]; the residue contains a *product*, $C_{24}H_{14}N_2S_5$ (*Bz_2* derivative, m.p. 218—222°), converted by hot 0·5N-NaOH into a *product*, $C_{24}H_{14}N_2S_4$. The product from (I), Mg, and EtBr does not react with S. E. W. W.

Cyclisation in the benzquinoline series. W. S. Johnson and F. J. Mathews (*J. Amer. Chem. Soc.*, 1944, **66**, 210—215).—δ-2-*Naphthylimino*-n-*pentan-β-one* (prep. from β-$C_{10}H_7$·NH_2, CH_2Ac_2, and $CaSO_4$ at 100°), m.p. 98·5—99°, in conc. H_2SO_4 at 100° gives 2 : 4-*dimethyl*-6 : 7-*benzquinoline*-x-*sulphonic acid* (I) (91%) and 2 : 4-dimethyl-5 : 6-benzquinoline (II) (4%), m.p. 128·5—129° (Reed, A., 1887, 681), in conc. H_2SO_4 at 60° gives 2 : 4-*dimethyl*-6 : 7-*benzquinoline* (III) (83%), dimorphic, m.p. 93—93·8° and 74·5—75·5° (Coombes, A., 1888, 968, m.p. 66—67°), and 2% of (I), and in HF at room temp. gives only (90%) (II). (II) is obtained in 70% yield by hydrolysis of (I) by 10% (vol.) H_2SO_4 at 220°. Structures are proved by the following reactions. With aq. $K_2Cr_2O_7$ in boiling AcOH, (II) gives 5 : 6-*phthaloyl*-2 : 4-*dimethylquinoline* (IV) (48%), m.p. 215—216°, photosensitive, which in $Na_2S_2O_4$ gives a deep purple vat, with Zn dust, Ac_2O, and H_2SO_4 gives the *quinol diacetate* (37%), m.p. 198—199°, and is very readily converted by $KMnO_4$ in 20% (vol.) H_2SO_4 into *o*-$C_6H_4(CO_2H)_2$. 1 : 2-$C_{10}H_6$Me·NH_2 (improved prep.), m.p. 49—50°, gives similarly δ-1-*methyl*-2-*naphthylimino*-n-*pentan-β-one*, m.p. 93—94·8°, which in HF gives 2 : 4 : 8-*trimethyl*-6 : 7-*benzquinoline* (V), m.p. 126·2—127°, oxidised as above to (IV). (II) and (V) are readily sulphonated [the SO_2H derivative of (V) is described], give yellow *hydrochlorides*, m.p. 324—325° (decomp.; uncorr.) and 295—296° (decomp.; uncorr.), respectively, and *picrates*, m.p. ~271—273° (decomp.; bath preheated at 250°) after darkening and 253—255° (decomp.; bath preheated at 240°) after darkening, respectively, and in C_6H_6 at room temp. or the b.p., respectively, give 5 : 8-maleic anhydride *adducts*, m.p. ~110—130° (decomp.) (impure) and 203·5—204·5°, respectively. 5 : 6-Benzquinoline (VI) and (III) give colourless anhydrides, are less readily sulphonated, and give tars with (:CH·$CO)_2O$. The reactivity of (IV) towards $KMnO_4$ is paralleled by that of 6 : 7-phthaloylquinoline. Structures are supported by absorption spectra (detailed), there being close resemblance between those of (*a*) (III), (V), and anthracene, and (*b*) (II), (VI), and 2 : 4-dimethyl-7 : 8-benzquinoline (prep. in 80—90% yield from the anil by H_2SO_4) (cf. also phenanthrene). Unless otherwise stated, m.p. are corr. R. S. C.

Thiobarbituric acids.—See B., 1944, III, 119.

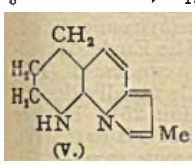
Preparation of *N*-mono- and unsymmetrically di-substituted piperazines. R. Baltzly, J. S. Buck, E. Lorz, and W. Schon (*J. Amer. Chem. Soc.*, 1944, **66**, 263—266).—Monosubstituted piperazine derivatives are obtained in good yield by the appropriate reagent (unless otherwise stated, 1 mol. in 50—100% MeOH or EtOH). CH_2ArCl gives 1-benzyl- (I), b.p. 127—130°/2 mm. (*dihydrochloride*, m.p. 253°), 1-*p*-anisylmethyl-, b.p. 150°/2·5 mm. [*dihydrochloride*, m.p. 263° (decomp.)], and 1-*p*-chlorobenzyl-piperazine, b.p. 140—142°/2·5 mm. [*dihydrochloride*, m.p. 296° (decomp.)]. Ph·[CH_2]$_3$·Br or *n*-$C_{12}H_{25}Br$ (0·7 mol.) gives 1-β-phenylethyl-, b.p. 150—152°/8 mm. (*dihydrochloride*, m.p. 252°), or 1-*n*-dodecyl-piperazine, b.p. 140°/0·25 mm. (*dihydrochloride*, decomp. >220°). $(CH_2)_2O$ (0·5—0·66 mol.) gives 1-β-hydroxyethylpiperazine, b.p. 122—123°/10 mm. (*dihydrochloride*, m.p. 189·5°). $ClCO_2Et$ in 95% EtOH at >50° (cooling) gives 1-carbethoxy- (hydrochloride, m.p. 145°) and 1 : 4-dicarbethoxy-piperazine, m.p. 49°. Ac_2O in AcOH at 48—54° gives 1-acetylpiperazine (hydrochloride, m.p. 183°). These products yield, by further reaction: 1-*benzoyl*-4-*phenyl*-, m.p. 245°, -4-β-*phenylethyl*-, m.p. 246°, -4-p-*chlorobenzyl*-, m.p. 265°, and -4-p-*anisylmethyl*-, m.p. 234°, 1-*phenylacetyl*-4-p-*anisylmethyl*-, m.p. 225°, and -p-*chlorobenzyl*-, m.p. 241°, *-piperazine hydrochloride*; 1-*benzyl*-4-*methyl*- (II), m.p. 250° (decomp.), -4-*ethyl*- (III), m.p. 250° (decomp.), -4-n-*dodecyl*-, decomp. >250° [*dimethiodide*, m.p. 225° (decomp.), of the derived base], -4-β-*hydroxyethyl*-, m.p. 225°, -4-3' : 4'-*dimethoxyphenacyl*-, decomp. 250—270°, and -4-3' : 4'-*dihydroxyphenacyl*- (IV), decomp. 255°, 1-p-*chlorobenzyl*-4-3' : 4'-*dihydroxyphenacyl*-, decomp. >200°, and 1-p-*anisyl*-4-3' : 4'-*dihydroxyphenacyl*- (V), m.p. 230—231°, *-piperazine dihydrochloride*; 1 : 4-*di*-n-*dodecylpiperazine dihydrochloride*; 1-β-*benzoyloxyethyl*-*piperazine dihydrochloride*, m.p. 208—210°, and -4-*ethylpiperazine dihydrochloride*, m.p. 245° (decomp.); 1-*benzyl*-4-β-*benzoyloxy*-, m.p. 245°, -4-β-p-*acetamidobenzoyloxy*-, m.p. 229° (decomp.), -4-β-p-*chlorobenzoyloxy*-, m.p. 242°, -4-β-p-*nitrobenzoyloxy*-, m.p. 236—237°, *-ethylpiperazine dihydrochloride*; 1-*benzyl*-4-β-p-*aminobenzoyloxyethylpiperazine trihydrochloride*, m.p. 258—260° (decomp.); (by means of PhNCO) 4-p-*chlorobenzylpiperazine*-1-*carboxylanilide hydrochloride*, m.p. 258° (decomp.); (by means of NH_2·CO·NH·NO_2) 4-p-*chlorobenzyl*-, m.p. 265°, 4-*benzyl*-, m.p. 238·5—239°, 4-β-*hydroxyethyl*-, m.p. 177°, and 4-β-*benzoyloxyethyl*-, m.p. 205° (decomp.), *-piperazine*-1-*carboxylamide hydrochloride*. SMe·C(NH_2):NH,HX and (I) in 65% EtOH give 1-*guanyl*-4-*benzylpiperazine sulphate*, m.p. 200° (decomp.), and (in EtOH, followed by MeI–MeOH) 4-*methiodide hydriodide*, m.p. 219—220° (decomp.). BrCN (1 mol.) and (I) (2 mols.) in Et_2O and then alone at 150—160° give 4 : 4'-*dibenzyl*-1 : 1'-*dipiperazinylcarbimide hydrobromide*, m.p. 229°. Heating (Cl·[CH_2]$_2$)$_2$O and (I) gives 4-*benzylmorpholine*-4' : 1-*spiropiperazinium* 1-*chloride* 4-*hydrochloride*, m.p. >280°. Hydrogenation (Pd–C) of (II) and (III) gives 1-*methyl*-, +H_2O, m.p. 110°, and 1-*ethyl*-*piperazine dihydrochloride*, m.p. 203—205°, respectively, and (PtO_2) of (IV) and (V) gives 1-*benzyl*-, decomp. >210°, and 1-p-*anisylmethyl*-4-β-*hydroxy*-3' : 4'-*dihydroxyphenylethylpiperazine dihydrochloride*, m.p. 175°. R. S. C.

Piperazines.—See B., 1944, II, 147.

Pyrazole synthesis. VII. Reactivity of carbonyl groups in asymmetric β-diketones. R. Fusco [with (Signa.) R. Pizzotti] (*Gazzetta*, 1942, **72**, 411—423).—Hexane-ββδ-dione in NaOMe–MeOH–Et_2O with *p*-NO_2·C_6H_4·NH·N:CBr·CO_2Et gives the *Et* ester (I), m.p. 174°, of 4-*propionyl*-1-p-*nitrophenyl*-5-*methylpyrazole*-3-*carboxylic acid* (II), m.p. 230° (decomp.). With HNO_3 (*d* 1·41), (I) or (II) gives 1-*p*-nitrophenyl-5-methylpyrazole-3 : 4-dicarboxylic acid (III) (A., 1939, II, 451). The expected isomeride of (I), Et 4-acetyl-1-*p*-nitrophenyl-5-ethylpyrazole-3-carboxylate, was not isolated; the mother-liquor in which it should be contained was, however, oxidised by HNO_3 to 1-p-*nitrophenyl*-5-*ethylpyrazole*-3 : 4-*dicarboxylic acid* (IV), m.p. 250°. Heptane-γε-dione, treated as above, gives the *Et* ester (V), m.p. 124°, of 4-*propionyl*-1-p-*nitrophenyl*-5-*ethylpyrazole*-3-*carboxylic acid* (VI), m.p. 169° (decomp.); either (V) or (VI) with HNO_3 gives (IV). Similarly heptane-ββδ-dione gives *Et* 4-n-*butyryl*-1-p-*nitrophenyl*-5-*methylpyrazole*-3-*carboxylate*, m.p. 114°, oxidised to (III), with a product, containing Et 4-acetyl-1-*p*-nitrophenyl-5-propylpyrazole-3-carboxylate, oxidised to 1-p-*nitrophenyl*-5-*propylpyrazole*-3 : 4-*dicarboxylic acid* (VII), m.p. 228°. Similarly nonane-δζ-dione gives *Et* 4-*butyryl*-1-p-*nitrophenyl*-5-*propylpyrazole*-3-*carboxylate*, m.p. 94°, oxidised to (VII). Octane-γε-dione (prepared either from $EtCO_2Et$ and COMePr or from $PrCO_2Et$ and COMeEt) gives a mixture of Et 4-propionyl-1-*p*-nitrophenyl-5-propyl- and 4-butyryl-1-*p*-nitrophenyl-5-ethyl-pyrazole-3-carboxylate, oxidised to (IV) + (VII). Phenoxyacetylacetone similarly treated gives a mixture of the *Et* ester, m.p. 144°, of 4-*acetyl*-1-p-*nitrophenyl*-5-*phenoxymethylpyrazole*-3-*carboxylic acid* (VIII), m.p. 147—148°, and Et 4-phenoxyacetyl-1-*p*-nitrophenyl-5-methylpyrazole-3-carboxylate (not isolated). With NaOBr, (VIII) gives 1-p-*nitrophenyl*-5-*phenoxymethylpyrazole*-3 : 4-*dicarboxylic acid*, m.p. 233° (with decomp. to the 4-*carboxylic acid*, m.p. 193—194°). The results suggest that the reactivity of ketonic groups is in the order CO·CH_2·OPh > Ac > COEt > COPr. The reaction between CH_2Ac·CO·CO_2R and $2NH_2OH$,HCl, if carried out in alkaline media, followed by heating with conc. HCl, gives mainly 3-methyl*iso*oxazole-5-carboxylic acid (through the dioxime?); in acid media the product is mainly 5-methyl*iso*oxazole-3-carboxylic acid. E. W. W.

Synthesis and hydrogenation of 1 : 8-naphthyridine homologues. E. Ochiai and K. Miyaki (*Ber.*, 1941, **74**, [*B*], 1115—1126).—Substitution of one ring of 1 : 8-naphthyridine by Me reduces the susceptibility of that ring to catalytic hydrogenation (cf. A., 1939, II, 452). 2 : 6-Diaminopyridine, CH_2Ac_2, and $ZnCl_2$ at 120—130° give 7-amino-, m.p. 220° (*Ac* derivative, m.p. 300°), and thence (NaNO$_2$–40% H_2SO_4) 7-hydroxy- (I), m.p. 251°, and ($POCl_3$; 140°) 7-chloro-2 : 4-dimethyl-1 : 8-naphthyridine (II), m.p. 146—147°. Boiling 20% NaOMe–MeOH converts (II) into 7-*methoxy*-2 : 4-*dimethyl*-1 : 8-*naphthyridine*, m.p. 65° (picrate, m.p. 188—189°). With H_2–Ni–kieselguhr in EtOH at 170—180°/110 atm., (I) yields 2 : 4-*dimethyl*-3 : 4-*dihydro*-1 : 8-*naphthyrid*-2-*one*, m.p. 175—180°. With H_2–Pd–C in 10% MeOH–KOH, (II) yields, first, 2 : 4-*dimethyl*- (III), m.p. 85—86° (*hydrochloride*, decomp. 240°; *picrate*, decomp. 204—206°; *methiodide*, +H_2O, m.p. 93—94°; *platinichloride*, decomp. 242—244°; *aurichloride*, decomp. 166—167°), and then 2 : 4-*dimethyl*-5 : 6 : 7 : 8-*tetrahydro*- (IV), m.p. 118° (picrate, m.p. 207°; *Ac* derivative, m.p. 42—43°), -1 : 8-*naphthyridine*, but with H_2–PdO–$CaCO_3$ and a trace of Pd–C in 5% KOH–MeOH gives only

(III) and with H_2–PtO_2 in AcOH or H_2–Raney Ni in *cyclo*hexane–EtOH at 120—190°/70 atm. gives only (IV). (IV) is unaffected by H_2–PtO_2 in AcOH at 110 atm. but with Na–EtOH gives dl-2 : 4-*dimethyldecahydro*-1 : 8-*naphthyridine*, m.p. 92—93° (*Ac*$_2$ derivative, b.p. 135—145°/0·02 mm.). CH_2Cl·COMe and (IV) in a little EtOH give an *adduct*, $C_{15}H_{22}O_2N_2Cl$, m.p. 181—182°, converted by aq. Na_2CO_3 into (IV) and the indolizine (V), a resin (blue Ehrlich test). 2 : 7-Dichloro-4-methyl-1 : 8-naphthyridine with H_2–PdO–$CaCO_3$ and a trace of Pd–C in 10% KOH–MeOH gives 4-*methyl*-1 : 8-*naphthyridine* (VI) (~70%), b.p. 147—148°/0·05 mm. (*picrate*, decomp. 204—205°; *perchlorate*, m.p. 180—181°), and some 2- or 7-*chloro*-4-*methyl*-1 : 8-*naphthyridine*, m.p. 104°.



(V.)

H_2-PtO_2 in AcOH reduces (VI) to 4-methyl-5 : 6 : 7 : 8- (VII) (4 parts), m.p. 102—103° (picrate, decomp. 248°; *Bz*, m.p. 105—106°, and *NO*$_2$-derivative, m.p. 217—218°; ? nitrate, m.p. 124—125°) (cf. Seide, A., 1927, 62), and -1 : 2 : 3 : 4-*tetrahydro*-1 : 8-*naphthyridine* (VIII) (1 part), m.p. 62—63° (*Bz* derivative, m.p. 86—87°). (VII) is unaffected by H_2–PtO_2 in AcOH at 65 atm., but with Na–C_5H_{11}·OH (not Na–EtOH) (VII) or (VIII) gives 4-*methyldecahydro*-1 : 8-*naphthyridine*, m.p. 87° (*picrate*, decomp. 210°). R. S. C.

Ketones, ketonic acids, and enol-lactones. III.—See A., 1944, II, 211.

Fission of indolacylpyridinium salts by alkalis. I. G. Sanna (*Gazzetta*, 1942, **72**, 357—363; cf. Babcock *et al.*, A., 1933, 74; Kröhnke, *ibid.*, 591).—With PhCHO and 25% NaOH, 2′-indolacylpyridinium bromide in aq. EtOH gives indole-2-carboxylic acid and phenacylpyridinium bromide (I). 3-*Methyl*-2-*indolacyl bromide*, m.p. 210° (Ag salt) (obtained from CH_2Br·COBr and the MgBr derivative of indole), with C_5H_5N gives 3′-*methyl*-2′-*indolacylpyridinium bromide*, m.p. 245°, which with NaOH and PhCHO gives 3-methylindole-2-carboxylic acid and (I). 2′-*Pyrrolacylpyridinium bromide*, m.p. 215°, similarly gives pyrrole-2-carboxylic acid and (I). E. W. W.

Indole α-ketoaldonitrones. I. Preparation of ketoaldehydes of the pyrrole and indole series. G. Sanna (*Gazzetta*, 1942, **72**, 363—370).—Indolacylpyridinium bromide (I) with PhNO in EtOH at −5° and N-NaOH gives 2-*aniloacetylindole* N′-*oxide* (I), m.p. 215°, converted by 10% NaOH into 2-indolylglyoxylic acid. With 0·1N-H_2SO_4, (II) gives 2-*phenylhydroxylaminoglycollylindole*, m.p. 93°, reconverted into (II) by keeping over P_2O_5. With NHPh·NH_2 in EtOH, (II) gives a mixture, m.p. 223°, of the α- and β-phenylhydrazones of indolylglyoxal (III). With NH_2Ph in EtOH, (II) gives the *bisaniline derivative*, m.p. 132°, of (III). With *p*-NO·C_6H_4·NMe_2 (IV), (I) gives 2-p-*dimethylaminoaniloacetylindole* N′-*oxide*, m.p. 228°, which with 25% H_2SO_4 (V) gives the hydrate of (III). 2′-Methyl-3′-indolacylpyridinium bromide and (IV) [PhNO ?] give 3-*aniloacetyl*-2-*methylindole* N′-*oxide*, m.p. 140°, which with (V) gives 3-*phenylhydroxylaminoglycollyl*-2-*methylindole*, which gives a mixture, m.p. 115°, of methylindolylglyoxalphenylhydrazones (additive product, m.p. 138°, with H_2SO_4), and a bisaniline derivative. 3′-Methyl-2′-indolacylpyridinium bromide and (IV) [PhNO ?] give 3-*aniloacetyl*-3-*methylindole* N′-*oxide*, m.p. 238°, which readily decomposes to 3-methylindole-2-carboxylic acid, and with (V) gives 3-*phenylhydroxylaminoglycollyl*-3-*methylindole*, m.p. 137°. E. W. W.

Synthesis of optical sensitisers. *iso*Cyanines substituted in position 4. III. V. A. Alexeeva (*J. Appl. Chem. Russ.*, 1943, **16**, 95—104; cf. B., 1938, 141).—11 *dyes* of the general formula 1 : 1′-dimethyl-4-X-*iso*cyanine iodide were prepared. Groups at X and respective m.p. are: Me (α), 233°; Me (γ), 255°; Et, 258° (decomp.); Ph, 246°; OH, 230°; OMe, 323° (decomp.); OEt, 233° (decomp.); ·NHPh, 281° (decomp.); Cl, 268° (decomp.) [6-Me derivative, 234° (decomp.)]; I, 273—274° (decomp.). Comparison of the methods of prep. described by Kaufmann (A., 1912, i, 503) and Hamer (*J.C.S.*, 1921, **119**, 1440) showed that the method of the former gave better yields. However, the OH-compound is obtainable only by Hamer's method and the OMe-compound only by Kaufmann's. Efforts to introduce the NH_2, NHMe, and NHPh·NH groups in position 4 were unsuccessful. V. B.

Triazines.—See B., 1944, II, 158, 198.

Chemistry of nucleotides. J. M. Gulland (*J.C.S.*, 1944, 208—217).—Tilden lecture, surveying progress over the past five years. Over 100 literature references are given. D. G.

***iso*Oxazole group. XI. Nitrodimethyl*iso*oxazole.** A. Quilico and C. Musante (*Gazzetta*, 1942, **72**, 399—411).—4-Nitro-3 : 5-dimethyl-*iso*oxazole (I) in dil. aq. NaOH with RN_2Cl gives, with ring-opening and -closing, 5-*benzeneazo*-2-*phenyl*- (II), m.p. 135—136°, and 5-p-*tolueneazo*-2-p-*tolyl*-, m.p. 165—166°, -4-*methyl*-2 : 1 : 3-*triazole* 3-*oxide*. In aq. $SnCl_2$–HCl, (II) gives 5-amino-2-phenyl-4-methyl-2 : 1 : 3-triazole, new m.p. 92—93° (*Ac* derivative, m.p. 148—149°; *Bz*$_2$ derivative, m.p. 144—145°; :*CHPh* derivative, m.p. 119—120°; ·O·*NHPh* derivative, m.p. 240°). With PhCHO in EtOH, followed by $NHEt_2$, (I) gives 4-*nitro*-5-*styryl*-3-*methyl*isooxazole (III), m.p. (*dibromide*, m.p. 167—168°), which on keeping, especially in sunlight, gives a *dimeride*, m.p. 201—202°. Similarly 4-*nitro*-5-p-*methoxy*-, m.p. 163—164°, -5-(3′ : 4′-*methylenedioxy*)-, m.p. 208—209°, -5-m-, m.p. 230—231°, and -p-*nitro*-, m.p. ~220°, and -5-*dimethylamino-styryl*-, m.p. 193—194°, and -5-*cinnamylidenemethyl*-3-*methyl*isooxazole, m.p. ~204—205°, are obtained from the corresponding aldehydes. With $SnCl_2$–HCl–EtOH, (III) gives 4-*amino*-5-*styryl*-3-*methyl*isooxazole (IV), m.p. 122° [*Bz* derivative (V), m.p. 176°; *Ac*$_2$ derivative, m.p. 111—112°; -*azo*-β-*naphthol*, m.p. 185—186°]. $KMnO_4$–$COMe_2$ oxidises (V) to 4-*benzamido*-3-*methyl*isooxazole-5-*carboxylic acid*, m.p. 176—177° (*Me* ester, m.p. 125—127°), which with conc. HCl gives the hydrochloride of 4-amino-3-methyl*iso*oxazole (cf. A., 1943, II, 74). The hydrochloride of (IV) with ice and aq. $NaNO_2$, followed by HCl, gives, after heating, 4-*chloro*-5-*styryl*-3-*methyl*isooxazole (VI), m.p. 75° (*dibromide*, m.p. 135°), with PhCHO and a yellow product (CHPh:CH·CO·CHCl·COMe ?), decomposed by NaOH to CHPh:CH·CO_2H. $K_2Cr_2O_7$–H_2SO_4 oxidises (VI) to 4-*chloro*-3-*methyl*isooxazole-5-*carboxylic acid*, m.p. 158—159° (Ag salt). E. W. W.

Behaviour of 4-nitro-derivatives of *iso*oxazole. Transformation into pyrazole derivatives. C. Musante (*Gazzetta*, 1942, **72**, 537—548).—4-Nitro-3 : 5-dimethyl*iso*oxazole with NHPh·NH_2 (I) in EtOH at the b.p. gives 4-nitro-1-phenyl-3 : 5-dimethyl- (II) and with N_2H_4 gives 4-nitro-3 : 5-dimethylpyrazole. (II) is reduced by $SnCl_2$–HCl to 4-*amino*-1-*phenyl*-3 : 5-*dimethylpyrazole*, m.p. (anhyd.) 38—40°, (+H_2O) 68° [*Ac*, m.p. 130—131°, and m-NO_2·C_6H_4·*CH*: derivative, m.p. 125—126°; -4-*azo*-β-*naphthol*, m.p. 188—189°; -4-*azoacetylacetone*, m.p. 118—119° (decomp.)]. 4-Nitro-5-methyl-*iso*oxazole (III) and (I) in EtOH give 4-nitro-5-amino-1-phenyl-3-methylpyrazole, which with $SnCl_2$–HCl, followed by NaOH and PhCHO, gives 4 : 5-*bis*(*benzylideneamino*)-1-*phenyl*-3-*methylpyrazole* (?), m.p. 161°, and when heated with 20% NaOH and acidified gives 4-nitro-1-phenyl-3-methylpyrazol-5-one (?). With N_2H_4, (III) gives 4-*nitro*-5-*amino*-3-*methylpyrazole*, m.p. 228° (*Ac* derivative, m.p. 180°; -5-*azo*-β-*naphthol*, darkens from 250°). 5-Methyl*iso*oxazole does not react with (III) or N_2H_4 under the above conditions, but with (III) at the b.p. for 15 hr. gives some 5-amino-1-phenyl-3-methylpyrazole. 4-Nitro-3-phenyl- and -3-methyl-*iso*oxazole give resinous products. 5-Phenyl-3-methyl*iso*oxazole with H_2SO_4–HNO_3 (*d* 1·40) gives 5-p-*nitrophenyl*-, m.p. 180° (oxidised to *p*-NO_2·C_6H_4·CO_2H), reduced to 5-p-*aminophenyl*-3-*methyl*isooxazole, m.p. 151—152° (*hydrochloride*, m.p. 250°; *Ac*, m.p. 241°, *Bz*, m.p. 235°, and *CHPh*:, m.p. 155°, derivatives; -*azo*-β-*naphthol*, m.p. 194°; -*azoacetylacetone*, m.p. 196—197°). E. W. W.

Heterocyclic syntheses. V. L. Panizzi (*Gazzetta*, 1943, **73**, 99—105).—3-Phenyl-5-dichloromethyl*iso*oxazole with NaOEt–EtOH at 140—160° gives 3-*phenyl*isooxazole-5-*aldehyde* (I), m.p. 75—76° [*oxime*, m.p. 165—166°; *phenylhydrazone*, m.p. 153—154°; p-*nitrophenylhydrazone*, m.p. 233—234° (decomp.); *anil*, m.p. 133—134°], oxidised by $K_2Cr_2O_7$–H_2SO_4 to the -5-*carboxylic acid*, m.p. 179—180°, also obtained with 3-phenyl*iso*oxazolyl-5-carbinol (*Bz* derivative, m.p. 74—75°) from (I) and hot 20% NaOH. With benzenesulphonhydroxamic acid and NaOH–EtOH, (I) gives 3-*phenyl*isooxazolyl-5-*carboxylhydroxamic acid*, m.p. 170° (decomp.); with CH_2N_2 in Et_2O, 5-*acetyl*-3-*phenyl*isooxazole, m.p. 103—104° [p-*nitrophenylhydrazone*, m.p. 228—229° (decomp.)]; with $MeNO_2$ and MeOH–NaOMe, α-*nitro*-β-3-*phenyl*-5-isooxazolylethylene, m.p. 87—88°. $CH(OEt)_2$·CO_2Et and $COMe_2$, with Na in Et_2O, give α*α*-*diethoxyacetylacetone*, b.p. 90—91°/4 mm. (*Cu* salt, m.p. 124—125°), which with NH_2OH gives 3-methyl*iso*oxazole-5-aldehyde. E. W. W.

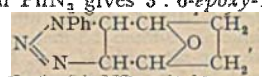
Morpholinomethyl derivatives of carbamide and substituted carbamides. W. I. Weaver, J. K. Simons, and W. E. Baldwin (*J. Amer. Chem. Soc.*, 1944, **66**, 222—225).—OBz·$[CH_2]_2$·NH_2,HCl and $CO(NH_2)_2$ (I) at 130—140° give β-*benzoyloxyethylcarbamide* (36%), m.p. 122—124°. Morpholinomethyl alcohol (II) (1) and (I) (1 mol.) at 80—90° give 92%, morpholine (III), (I), and paraformaldehyde (IV) (equiv. amounts) in boiling dioxan give 84%, and methylenebismorpholine and (I) in boiling dioxan give 33%, of *morpholinomethylcarbamide* (V), m.p. 162—163°. s-*Di*(*morpholinomethyl*)*carbamide* (VI), m.p. 163—164°, is obtained from (I) by 2 mols. of boiling (II) (95%), and from (I) (1 mol.), (III) (2), and (IV) (2 mols.) in boiling dioxan (90% yield). Prep. of (VI) (60% yield) from $CO(CH_2$·$OH)_2$ by (III) (excess) in boiling H_2O and failure of NHR·CO·NHR′ to condense with (II) proves the symmetrical nature of (VI) and the products named below. Hot 10% NaOH hydrolyses (V) or (VI) to (III); Zn–HCl reduces (V) or (VI) to 1-methylmorpholine, which is also obtained with (I) from (V) by H_2–PtO_2 in EtOH. Ac_2O and (V) at 100° give acetylmorpholine (VII) and a *substance*, ? $[·CH_2·N·CO·N·CH_2·]_x$, m.p. 235—236°. In AcOH, (V) and (VI) give *picrates*, m.p. 162—163·3° and 163—164°, respectively, but in EtOH or H_2O give picrates which gradually decompose to regenerate (V) and (VI) when recrystallised. (V) yields, usually in H_2O, N-*morpholinomethyl*-N′-*methyl*-, m.p. 124·4—125·4°, -*ethyl*-, m.p. 109·6—110·8°, -n-, m.p. 89·2—90°, and -iso-*propyl*-, m.p. 126·8—128°, -*allyl*-, m.p. 104—105°, -n-, m.p. 109—109·6°, -iso-, m.p. 112—112·6°, -sec.-, m.p. 111—112°, and -tert.-*butyl*-, m.p. 137·8—138·8°, -sec.-, m.p. 107—108·4°, and -tert.-*amyl*-, m.p. 107·4—109°, -cyclo*hexyl*-, m.p. 138—139°, -β-*hydroxyethyl*-, m.p. 118—119·8°, and -β-*benzoyloxy*-

methyl-, m.p. 125·4—127·6°, *-carbamide*, N-*phenyl-*, m.p. 149·4—149·8° (picrate, m.p. 156—158°), N-*benzyl-*, m.p. 149·3—149·8°, and N-*acetyl-* (**VIII**), m.p. 161—161·8° (picrate, m.p. 195°), -N′-*morpholinomethylcarbamide*. Good yields of *morpholinomethylthiocarbamide*, m.p. 141·4—142°, *succin-*, m.p. 109·6—110·4° (picrate, m.p. 188—189°), and *phthal-morpholinomethylimide*, m.p. 117·8—118·8° (picrate, m.p. 205°), *benzene-*, m.p. 81·6—82·6°, and p-*toluene-sulphonmorpholinomethylamide*, m.p. 109·6—111·2°, are obtained. $(RCO)_2O$ and (**VIII**) at 100° give N-*acetyl*-N′-*acetoxy-*, m.p. 144·6—145·2° [and (**VII**)], and -N′-*butyroxy-methylcarbamide*, m.p. 116·8—117°. 1-*Carbamylmorpholine*, m.p. 131·6—133°, is also prepared. R. S. C.

Condensation of xanthhydrol with hydroxyquinolines. (Signa.) L. Monti and M. Delitala (*Gazzetta*, 1942, **72**, 520—524).—4-Hydroxy-2-methylquinoline in AcOH with xanthhydrol (**I**) in EtOH gives 4-*hydroxy*-3-*xanthyl*-2-*methylquinoline*, m.p. 300—305° (decomp.). 4-*Hydroxy*-3-*xanthyl*-2 : 8-*dimethyl-*, decomp. from 290—292°, 4-*hydroxy*-6-*methoxy*-3-*xanthyl*-2-*methyl-*, decomp. from 295—300°, 3-*hydroxy*-4-*xanthyl-*, m.p. 240—242° (Ac derivative, m.p. 190—192°), 5-*hydroxy*-8-*xanthyl-*, decomp. 195—200°), 6-*hydroxy*-5-*xanthyl-*, m.p. 260—262° (Ac derivative, m.p. 214—215°), 8-*hydroxy*-5-*xanthyl-*, m.p. 193—195°, and 2 : 7-*dihydroxy*-8-*xanthyl*-4-*methyl-quinoline* (Ac derivative, decomp. from 205—210°, m.p. 215—220°) are obtained similarly. 2-Hydroxy-4-methyl- and 2-hydroxy-6-methoxy-4-methyl-quinoline do not condense with (**I**), nor do alkyloxy- or acetoxy-quinolines. An improved prep. of 2 : 7-dihydroxy-4-methylquinoline from *m*-$NH_2{\cdot}C_6H_4{\cdot}OH$ and $CH_2Ac{\cdot}CO_2Et$ (C_5H_5N) is described. E. W. W.

Thiazoles.—See B., 1944, II, 131.

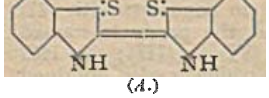
Cyanines etc.—See B., 1944, II, 160.

3 : 6-Epoxy*cyclo*hexene from furan and ethylene. W. Nudenberg and L. W. Butz (*J. Amer. Chem. Soc.*, 1944, **66**, 307—308).—Furan, C_2H_4, and a trace of quinol at 150—155°/1100—1200 lb. (cf. A., 1942, II, 167) give 3 : 6-epoxy-Δ^1-*cyclo*hexene (5—8%), b.p. 118—119°, which with PhN_3 gives 3 : 6-*epoxy*-1′-*phenyl*-1′ : 2′ : 3′-*triazolino*cyclo*hexane*,  m.p. 166—167° (corr.), and with H_2–PtO_2 in MeOH and then Ac_2O–$ZnCl_2$ yields 1 : 4-diacetoxy*cyclo*hexane. R. S. C.

Condensation reactions of xanthhydrol [with heterocyclic compounds containing active NH groups]. (Signa.) L. Monti (*Gazzetta*, 1942, **72**, 515—520).—Xanthhydrol (**I**) and 4-hydroxyquinazoline in AcOH give 3-*xanthyl*-4-*quinazolone*, m.p. 198—200°. 2-Hydroxybenziminazole with (**I**) in AcOH–EtOH gives 1-*xanthyl-*, m.p. 268—283—285°. 2-Thiolbenziminazole and (**I**) in AcOH–EtOH give 270°, or with excess of (**I**) gives 1 : 3-*dixanthyl-benziminazolone*, m.p. (1 : 1) 1-*xanthyl-*, m.p. 252—254°, or (1 : 2) 1 : 3-*dixanthyl-benziminazolthione*, m.p. 260—262°. Rhodanine and (**I**) give 3-*xanthylrhodanine*, m.p. 190—192°. E. W. W.

Synthesis of vitamin-B_1. A. I. Gravin (*J. Appl. Chem. Russ.*, 1943, **16**, 105—117).—From a survey of the literature it is concluded that a suitable industrially applicable method for the synthesis of vitamin-B_1 is the condensation (in $CHBr_3$) of 4-amino-2-methyl-5-bromomethylpyrimidine hydrobromide (**I**) with 4-methyl-5-β-hydroxyethylthiazole (**II**). (**I**) is obtained by condensing acetamidine with Et formylsuccinate, and converting the product by P_2O_5 into the chloride and then, by NH_3, into 4-amino-2-methylpyrimidyl-5-acetamide. This is converted (Hofmann) into the amine and then (HNO_2) the OH-derivative; HBr then gives (**I**). (**II**) is obtained by condensing γ-chloro-α-acetoxypentan-δ-one with $(NH_4)_2COS_2$, yielding 2-thiol-4-methyl-5-β-acetoxyethylthiazole, which is oxidised by H_2O_2 to (**II**). The entire synthesis is divided into 17 stages, for each of which yields and experimental details are given. V. B.

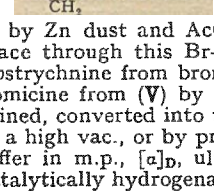
Action of sulphur on heterocyclic compounds : indole and pyrrole thio-compounds. (Signa.) L. Raffa (*Gazzetta*, 1942, **72**, 549—557).—3-Methylindole and S at 115—125° give a *substance*, $C_{27}H_{23}N_3S_2$, probably 2 : 3-*di*-(2′ : 2″-*indolylsulphido*)-3 : 3′ : 3″-*trimethylindole*, m.p. 215—217° (decomp.) (Ag_2 derivative; *hydrochloride*, decomp. 188°). Indole and S at 190—200° give a green *compound* [regarded as 3 : 3′-(dithio)indigo (*A*), 2 : 2′-(dithio)*iso*-indigo, or 3 : 2′-(dithio)indirubin] (Bz_2 derivative), which on alkali-fusion gives *o*-$NH_2{\cdot}C_6H_4{\cdot}CO_2H$. Pyrrole and S at 115—125° give a *sulphurised pyrrole-black*, $(C_{12}H_{12}N_2S)_x$. E. W. W.

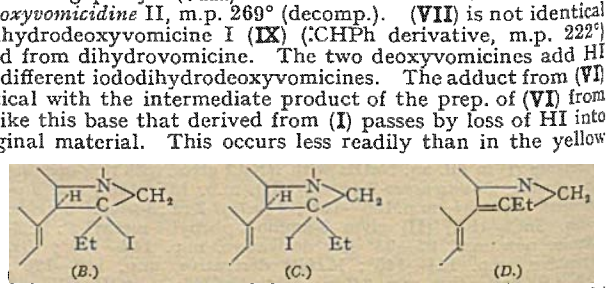

(*A.*)

VII.—ALKALOIDS.

***Strychnos* alkaloids. XXVIII. Emde degradation of vomicine.** H. Wieland and W. Weisskopf [with, in part, R. Huisgen] (*Annalen*, 1943, **555**, 1—9).—Treatment of vomicinium methosulphate in 3N-AcOH containing NaOAc with Na–Hg at 60—70° leads to methylvomicine I (**I**), m.p. 232·5°, $[\alpha]_D$ +156·5°, and *methylvomicine* II (**II**), m.p. 240°, $[\alpha]_D$ +126° [*methiodide*, m.p. 206° (decomp.)], which gives a violet colour with $FeCl_3$ and suffers opening of the lactam ring when boiled with 20% KOH–MeOH. (**II**) contains 1 OMe and 1 NMe and is hydrogenated (PtO_2 in 4N-AcOH) to a H_4-derivative (*picrate*, m.p. 142—144°). (**II**) is demethylated by boiling 40% HBr to a *substance*, $C_{22}H_{27}O_4N_2Br$, m.p. >300°. (**I**) in 60% H_2SO_4 is reduced at a Pb cathode to *methylvomicidine* I, m.p. 230° (decomp.), becomes brown at >225°. The Emde degradation of the methiodide of (**I**) leads to *dimethylvomicine* I (**III**), m.p. 92° [*perchlorate*, m.p. 250° (decomp.)], which is rapidly decomposed without yielding a cryst. product by boiling 25% HBr or HCl. Boiling 40% HBr transforms (**I**) into the OH-*base* (**IV**), $C_{22}H_{26}O_4N_2$, m.p. 272° (*methiodide*, m.p. ~215°; *benzoate*, m.p. ~227°, sinters at 218°; *CHPh* derivative, m.p. 208—210°), in which OH is not *tert.* since (**IV**) is converted by Ac_2O at 180° into a non-cryst. acetate which regenerates (**IV**) when hydrolysed, can be distilled almost unchanged at 290°/high vac., and is indifferent to $SOCl_2$. Demethylated (**I**) is hydrogenated (PtO_2 in 2N-AcOH) to a compound which gives a *picrate*, m.p. 218°. Electrolytic reduction of (**III**) at a Pb cathode leads to *dimethylvomicidine* I, m.p. 236° (slight decomp.). The methiodide of (**III**) is transformed by KOH–MeOH at 110—120° into NMe_3 and an isomeric *dimethylvomicine methiodide*, m.p. 278° (slight decomp.). Emde degradation of the methiodide of (**II**) gives partly (**II**) and partly *dimethylvomicine* II (**V**), m.p. 184°, the lactam ring of which is readily opened by KOH–MeOH. (**V**) is hydrogenated (PtO_2 in 2N-NaOH) to a H_2-derivative, m.p. 165° [*methiodide*, m.p. 290° (decomp.)], and is reduced at a Pb cathode to *dimethylvomicidine* II, m.p. 236°. H. W.

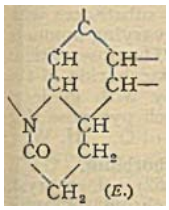
***Strychnos* alkaloids. XXIX. Constitution of deoxyvomicine.** R. Huisgen and H. Wieland (*Annalen*, 1943, **555**, 9—25).—Colourless deoxyvomicine (**I**) is converted by boiling HBr–AcOH containing red P into *tert.*-bromodihydrodeoxyvomicine (**II**), decomp. 235°, becomes discoloured at >165°, re-converted into (**I**) by Zn dust in AcOH but transformed by these reagents in boiling MeOH into *dihydrodeoxyvomicine* (**III**), m.p. 209°, $[\alpha]_D$ +245° in $CHCl_3$, +221° in EtOH. This is also obtained through a Br-base from dihydrovomicine and HBr but could not be derived by direct hydrogenation of (**I**). (**II**) is re-converted into (**I**) by boiling C_5H_5N or by anhyd. NaOAc in boiling AcOH. (**I**) has therefore the partial formula *A* (R = CHMe) and appears to be the deoxy-derivative of *iso*vomicine (**IV**), formed from vomicine (**V**) under the influence of HBr and having the structure *A* (R = $CH{\cdot}CH_2{\cdot}OH$). Actually (**IV**) is converted into (**I**) by replacement of OH by Br, which is exchanged for H by Zn dust and AcOH. The formation of (**IV**) from (**V**) takes place through this Br-compound in analogy to the production of *iso*strychnine from bromodeoxystrychnine. In the prep. of deoxyvomicine from (**V**) by HI in AcOH the yellow variety (**VI**) is obtained, converted into the more stable (**I**) by alkalis, by distillation in a high vac., or by protracted heating with solvents. (**VI**) and (**I**) differ in m.p., $[\alpha]_D$, ultra-violet absorption, and reactions but are catalytically hydrogenated to the saturated base $C_{22}H_{30}O_2N_2$ among other products. The isomerism of (**I**) and (**VI**) appears to be caused by differing arrangement of the double linkings, which in (**I**) is as shown in *A* since on ozonisation (**I**) gives >80% of the quantity of MeCHO (as dinitrophenylhydrazone) calc. for 1 mol. (**V**) also gives MeCHO but more slowly and in much lower yield. The double linking in the lactam ring is $\beta\gamma$ to CO (not $\alpha\beta$ as assumed previously) since (**I**) contains a reactive CH_2. Whereas (**V**) and strychnine only condense with PhCHO under the influence of alkali, this condensation occurs with (**I**), (**III**), and (**IV**) in presence of piperidine (*benzylidenedeoxyvomicine* has m.p. 198—199°). (**VI**) is not immediately derived from (**V**) and HI, which directly yield *iododihydrodeoxyvomicine* II *hydriodide*, m.p. 214° (decomp.). Attempts to isolate the free base are accompanied by elimination of HI and formation of (**VI**). Replacement of I by H by use of Zn dust in cold HI affords *dihydrodeoxyvomicine* II (**VII**), m.p. 168°, $[\alpha]_D^{20}$ +345° in $CHCl_3$ [*hydrochloride* (**VIII**), m.p. 235° (decomp.) after becoming pink]. (**VIII**) is reduced at a Pb cathode to *dihydrodeoxyvomicidine* II, m.p. 269° (decomp.). (**VII**) is not identical with dihydrodeoxyvomicine I (**IX**) (:CHPh derivative, m.p. 222°) obtained from dihydrovomicine. The two deoxyvomicines add HI to give different iododihydrodeoxyvomicines. The adduct from (**VI**) is identical with the intermediate product of the prep. of (**VI**) from (**V**). Like this base that derived from (**I**) passes by loss of HI into the original material. This occurs less readily than in the yellow


(*A.*)


(*B.*) (*C.*) (*D.*)

series but still so easily (with NaOAc) that there can be no doubt about the attachment of I to *tert.* C. The isomerism of the hydr-

iodides is epimeric (cf. *B* and *C*). That derived from (**VI**) is *C*, thus leading to *D* from (**VI**). (**III**) is hydrogenated (PtO_2 in 2N-AcOH) to *tetrahydrodeoxyvomicine* (**X**), m.p. 246—247° [*methiodide*, m.p. 222° (decomp.), $[\alpha]_D^{21}$ +210° in $CHCl_3$; *CHPh* derivative, m.p. 247°, obtained by use of 20% NaOH but not of piperidine], and *deoxyvomicine* B (**XI**), m.p. 185—186°, $[\alpha]_D^{20}$ +270° in $CHCl_3$. The change proceeds more rapidly in glacial AcOH but leads exclusively to (**X**), which is also obtained by hydrogenation (PtO_2 in EtOH) of (**II**) and primary bromodihydrodeoxyvomicine. (**X**) and (**XI**) are electrolytically reduced in 60% H_2SO_4 at a Pb cathode to *tetrahydroxyvomicidine-A*, m.p. 250—251° (decomp.), softens at 240°, and *-B*, m.p. (indef.) ~200°. The isomerism of (**X**) and (**XI**) depends on the union of the carbocyclic and heterocyclic 6-membered rings (cf. *E*) in the *cis*- or *trans*-position. Fission of the oxide ring of (**I**) by H halides proceeds similarly with (**V**), strychnine (**XII**), brucine, and their H_2-bases. An apparent exception appears to be afforded by (**XII**), which with HI under drastic conditions gives tetrahydrodeoxystrychnine. Under milder, precisely specified conditions (**XII**) gives deoxystrychnine, m.p. 197—198°, softens at 195—196°. (**XII**) has a semicyclic double linking and when ozonised affords MeCHO (as 2 : 4-dinitrophenylhydrazone) in 90% yield. apo-*Strychnine*, $C_{21}H_{20}ON_2$, m.p. 242—244°, is obtained as by-product of the action of HBr on (**XII**). H. W.



Physostigmine [eserine] and related substances. IV. Chemical studies on physostigmine breakdown products and related epinephrine derivatives. S. Ellis (*J. Pharm. Exp. Ther.*, 1944, 79, 364—372).—Methods are described for the prep. of eseroline, rubreserine (**I**), eserine-blue, eserine-brown, and adrenochrome (**II**). Measurements of absorption spectra of (**I**), (**II**), and 2-iodoadrenaochrome indicate that (**I**) contains a substituted 2 : 3-dihydroindole-5 : 6-quinone group and is thus structurally related to (**II**), the oxidation product of adrenaline. F. R. S.

Structure of monocrotaline. XI. Proof of the structure of retronecine. R. Adams and N. J. Leonard (*J. Amer. Chem. Soc.*, 1944, 66, 257—263; cf. A., 1944, II, 147).—Retronecine is proved to be 7-hydroxy-1-hydroxymethylpyrrolizidine, $CH_2<\begin{matrix}CH(OH)\cdot CH\cdot C(CH_2\cdot OH)\\ CH_2\text{——}N\text{·}CH_2\end{matrix}>CH$, by synthesis of retronecanone (**II**). Adding molten *m*-$NO_2\cdot C_6H_4\cdot$COCl to 4-methylpiperidine (prep. from 4-methylpyridine by H_2–Raney Ni at 210°/150—300 atm.), b.p. 126—129°, and aq. NaOH at 35—40° gives 1-m-*nitrobenzoyl-4-methylpiperidine*, m.p. 72—73°, oxidised by boiling aq. $KMnO_4$ to dl-δ-m-*nitrobenzamido-β-methyl*-n-*valeric acid* (**III**) (67%), m.p. 103—105°, which with quinidine in EtOH–Et_2O gives the l- (**IV**) (36%) and d-*acids*, m.p. 113—114°, $[\alpha]_D^{30}$ −5·0±0·2°, +5·3±0·2°, respectively, in EtOH [quinidine salt of (**IV**), m.p. 125—126·5° (corr.), $[\alpha]_D^{3}$ +111·5° in EtOH]. Br and red P at 90° convert (**III**) into the crude, oily α-Br-acid (**V**) with some dl-3 : 3-*dibromo*-1-m-*nitrobenzoyl-4-methyl-2-piperidone* (**VI**), m.p. 152—153° (corr.). Boiling Ac_2O cyclises (**III**) to 1-m-*nitrobenzoyl-4-methyl-2-piperidone* (**VII**), m.p. 102—103°, which with Br and a trace of PCl_3 in $CHCl_3$ in light yields (**VI**). (**IV**) yields similarly l-(**VII**), m.p. 167—168° (corr.), $[\alpha]_D^{30}$ −20·2±0·2° in C_5H_5N, and oily *l*-(**V**). In N-NaOH at 37°, *dl*- or *l*-(**V**) gives *dl*- and *l*-1-m-nitrobenzoyl-3-methylpyrrolidine-2-carboxylic acids, oils, which with boiling 3N-aq. HCl and then boiling HCl–EtOH yield *Et* dl-, b.p. 90—91·5°/17·5 mm. (*picrate*, m.p. 112·5—114°), and l-3-*methylpyrrolidine-2-carboxylate*, b.p. 97—98°/23 mm. $[\alpha]_D^{28}$ ~0° in EtOH, which add $CH_2{:}CH\cdot CO_2Et$ (in presence of a trace of quinol) at the b.p. to yield *Et* dl- (97%), b.p. 163·5—165·5°/18 mm. (*picrate*, m.p. 98—99°), and l-β-2-*carbethoxy*-3-*methyl*-1-*pyrrolidinopropionate*, b.p. 170—171°/25 mm., $[\alpha]_D^{30}$ −34·9±0·5° in EtOH. Cyclisation by K in xylene–C_6H_6 then affords dl-, b.p. 96·5—98°/18 mm. [*picrate*, m.p. 189—190° (corr.); *methiodide*, m.p. 149·5—150·5° (corr.)], and *l*-7-keto-1-methylpyrrolizidine [=(**II**)] [identified as oxime, m.p. 166—167° (corr.), $[\alpha]_D^{32}$ −77·3±1·5° in EtOH, oxime picrolonate, m.p. 209—211° (corr.), l-*menthhydrazide*, m.p. 175·5—176·5° (corr.), $[\alpha]_D^{28}$ −83·2±0·5° in EtOH, and other derivatives, and by conversion into retronecanol methiodide acetate, m.p. 215—216° (corr.) (lit. 207—208°), $[\alpha]_D^{28}$ −87·4±1·0° in MeOH]. H_2–PtO_2 reduces (**II**) in EtOH to an oily isomeride, $[\alpha]_D^{33}$ −9·5° in EtOH [*picrate*, m.p. 218—219° (corr.; decomp.); *acetate methiodide* (**VIII**), m.p. 210—212° (corr.), $[\alpha]_D^{26}$ +7·5° in EtOH], of retronecanol and in EtOH + a little conc. HCl gives an isomeride {*picrate*, m.p. 230—232° (corr.; decomp.); *acetate picrate*, m.p. 178·5—179·5° (corr.), and methiodide [=(**VIII**)], m.p. 210·5—211·5° (corr.)}. Hydrogenation (PtO_2) of (**VII**) in EtOH yields a *dl*-7-hydroxy-1-methylpyrrolizidine [*picrate*, softens 210°, m.p. 218·5—219·5° (corr.; decomp.); *picrolonate*, m.p. 182·5—183·5° (corr.)]. R. S. C.

VIII.—ORGANO-METALLIC COMPOUNDS.

Amidino-arsenicals. II. Tervalent arsenicals. F. Linsker and M. T. Bogert (*J. Amer. Chem. Soc.*, 1944, **66**, 191—192; cf. A., 1943, II, 284).—*p*-CN·$C_6H_4\cdot AsO_2H_2$ in 2N-NaOH with, successively, KI, H_2SO_4 (excess), and SO_2 at >10° gives p-*cyanophenylarsinous acid* (**I**) (85%), softens 230°, m.p. 234° (decomp.; corr.), also obtained [80%, m.p. 230—240° (decomp.)] from *p*-$NH_2\cdot C_6H_4\cdot AsO,2H_2O$, m.p. 98° (decomp.) [lit. m.p. 100° (decomp.)], by treating the derived diazonium chloride with $CuSO_4$–KCN, purification being by dissolution in N-NaOH and pptn. by NH_4Cl. HCl–EtOH–Et_2O converts (**I**) at 0° into the *imino-ether hydrochloride* (95%), softens 150°, m.p. 152° (decomp.), hydrolysed by 10% NH_3–EtOH at 60° to p-*amidinophenylarsinous acid hydrochloride*, m.p. 210° (decomp.), whence HCl or HBr at 0° yields *dichloro*-p-*amidinophenylarsine hydrochloride*, sinters 202°, m.p. 208° (decomp.), or the *dibromoarsine hydrobromide*, m.p. 219° (decomp.), respectively. p-*Arsinibenzimino ether hydrochloride*, m.p. 130° (decomp.), is also described. R. S. C.

Preparation of phenylarsinoxides. VI. *p*-Arsinoxidobenzoylcarbamide and related compounds. H. G. Steinman, G. O. Doak, and H. Eagle. **VII. *p*-Arsinoxido-compounds containing amide groups. VIII. Arsonic acids and arsinoxido-compounds containing the azo-linking.** G. O. Doak, H. G. Steinman, and H. Eagle (*J. Amer. Chem. Soc.*, 1944, 66, 192—194, 194—197, 197—200; cf. A., 1942, II, 337).—VI. *p*-COCl·$C_6H_4\cdot AsCl_2$ (**I**) does not yield *p*-COCl·$C_6H_4\cdot$AsO by any direct method; with Na urethane in Et_2O (not C_6H_6 or C_5H_5N) it gives *Et di*-p-*arsinoxidobenzoylcarbamate*. p-*Nitrobenzoylisocarbimide* (**II**) [prep. from *p*-$NO_2\cdot C_6H_4\cdot$COCl (**III**) by AgNCO in boiling C_6H_6], m.p. 209—210°, with $NH_2\cdot[CH_2]_2\cdot OH$ in C_6H_6 gives N-p-*nitrobenzoyl*-N′-*β-hydroxyethylcarbamide* (30%), m.p. 186—187°, hydrogenated (method: Stevinson *et al.*, A., 1935, 1139, in this and similar cases) to the NH_2-derivative, m.p. 230·5—231·5°, which yields (Bart) the p-AsO_3H_2-, m.p. 238—238·5° (decomp.), and thence (SO_2) the amorphous p-*AsO*-derivative (not obtainable from *p*-$AsO_3H_2\cdot C_6H_4\cdot$COCl by AgNCO etc.). $NH_2\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH$ and (**II**) give N-p-*nitrobenzoyl*-N′-*βγ-dihydroxy*-n-*propylcarbamide* (22%), m.p. 197—199°, whence H_2–Raney Ni yields only *p*-$NH_2\cdot C_6H_4\cdot CO\cdot NH_2$. Boiling (**II**) and $CO(NH_2)_2$ in C_6H_6 gives α-p-*nitro*- (50%), m.p. 203—205°, and thence α-p-*amino*- (90%), sinters ~270°, and α-p-*arsono-benzoylbiuret*, m.p. >360°. Boiling $AsCl_2\cdot C_6H_3Me\cdot$COCl with $CO(NH_2)_2$ and hydrolysing the product gives p-*arsinoxido-*" α "-*toluoylcarbamide*, decomp. >272°. N-p-*Arsinoxyoxidoanilinoacetcarbamide*, amorphous, m.p. 166—168° (decomp.), is obtained by reducing the AsO_3H_2-compound by SO_2. $NH_2\cdot CO\cdot CH_2\cdot NH_2$,HCl (**IV**) and (**III**) in aq. $NaHCO_3$ give p-*nitrobenzamidoacetamide*, m.p. 239—240° (decomp.), reduced to the p-NH_2-derivative, m.p. 228° (decomp.) (*sulphate*, decomp. >250°), whence the Bart reaction yields the p-AsO_3H_2-derivative, m.p. 211—213° (decomp.); this does not yield the p-*AsO*-derivative, decomp. >285°, which is obtained from (**I**) and (**IV**) in aq. Na_2CO_3. *N*-Glycylglycine and (**I**) in N-KOH give amorphous N-p-*arsinoxidohippurylglycine*, decomp. >220°, which, by way of the *Ag* salt, yields the amorphous *Me* ester, decomp. >240°, and thence the *amide*, decomp. >240°. β-Alanine amide (prep. from $CN\cdot CH_2\cdot CO\cdot NH_2$ by H_2–Raney Ni in EtOH), m.p. 149°, gives similarly β-p-*arsinoxidobenzamidopropionamide*, m.p. 283—285° (decomp.). Glycine amide yields similarly p-*arsenoxido-*" α "-*toluamido-*, m.p. 133° (decomp.), and p-*arsenoxidobenzenesulphonamido-acetamide*, amorphous, m.p. 193—195° (decomp.). Amorphous N-p-*arsono-*, m.p. 326·5°, and N-p-*arsinoxido-benzoylcarbamide*, m.p. 270—271°, are also described.

VII. *m*-5-Xylidine gives (Bart) m-5-*xylylarsonic acid* (18%), m.p. 222—223°, oxidised by $KMnO_4$ to the *salt*, KHX,H_2X [X = $(CO_2H)_2C_6H_3\cdot AsO_3$], decomp. >300°, whence PCl_5–PCl_3 and then cold, aq. NH_3 yields 5-*arsenoxidoisophthalic acid*, $+2H_2O$, amorphous, m.p. 224—225°. The derived Me_2 ester, m.p. 255°, with NH_3 at 100° gives the *diamide*, $+H_2O$, a glass, softens 75°. 5-*Nitro*-o-*tolylarsonic acid* (prep. by Scheller–Bart reaction), m.p. 240°, gives 5-nitro- and thence 5-*amino*-2-*arsonobenzoic acid*, m.p. >360°, which affords (method: Doak *et al.*, A., 1941, II, 272, but using CuCN) impure 5 : 1 : 2-CN·$C_6H_3(CO_2H)\cdot AsO_3H_2$, decomp. >300°, whence 30% H_2O_2 yields 6-*arsono-*, m.p. 347·5°, and thence 6-*arsinoxidoisophthalamic acid*, $+H_2O$, m.p. 236·5—237·5°. Similarly are prepared 4-*nitro*-o-*tolylarsonic acid*, m.p. 235—236°, 4-amino-, $+H_2O$, decomp. 220° [lit., anhyd., m.p. 120° (decomp.)], and 4-*cyano*-2-*arsonobenzoic acid*, decomp. >351°, 4-*arsono-*, m.p. >360°, and 4-*arsinoxido-terephthalamic acid*, m.p. 221·5—222·5°. 2 : 1 : 4-$NO_2\cdot C_6H_3(CO_2H)\cdot AsO_3HK$ gives (PCl_5–$POCl_3$) the acid chloride, converted by cold, aq. NH_3 into 2-*nitro*-4-*arsinoxidobenzamide*, m.p. 162—163° (decomp.), which with 30% H_2O_2 gives 3-*nitro*-4-*carbamylphenylarsonic acid*, decomp. >270°. This is hydrogenated to 4-*carbamyl*-m-*arsanilic acid*, decomp. >230°, reduced by SO_2 to the *AsO*-compound (**V**), $+1·5H_2O$, m.p. 177—178°, which is better obtained from 4 : 2 : 1-$AsO\cdot C_6H_3(NH_2)\cdot CO_2Me$ by aq. NH_3 at 90°. The amorphous *Ac* derivative, $+H_2O$, m.p. 263—264° (decomp.), of (**I**) is obtained therefrom by Ac_2O but not by reduction of the AsO_3H_2-compound. 2 : 4 : 1-$NHAc\cdot C_6H_3(AsO_3H_2)\cdot CO_2H$ could not be converted into the benzamide derivative. 4-*Arsinoxido-*, $+H_2O$, m.p. >360°, is obtained by reducing 4-arsono-salicylamide. *Me* 5-*arsonosalicylate*, softens 193°, suffers fission by NH_3 at 100° but at 0° gives 4-*hydroxy*-3-*carbamylphenylarsonic acid*, decomp. >330°, and thence 5-*arsinoxidosalicylamide*, $+0·5H_2O$, m.p. 222—223°.

4-Hydroxy-5-carbamyl-m-arsanilic acid (similarly prepared) gives an unstable *dichloroarsine hydrochloride*, m.p. 177—178°.
p-CN·C_6H_3·AsO_3H_2 with SO_2–HI–H_2SO_4 gives p-*arsinobenzonitrile*, amorphous, m.p. 195·5—197·5°, whence HCl–Et_2O–95% EtOH at 0° gives p-*dichloroarsinobenzimino Et ether hydrochloride*, +H_2O, m.p. 141°, hydrolysed by $NaHCO_3$ to p-*arsinoxidobenzimino Et ether*, +H_2O, amorphous, m.p. 184·5—185°. *p*-$AsCl_2$·C_6H_4·COCl (**VI**) with 3 : 1 : 2-NH_2·CH_2·CH(OH)·CH_2·OH and Na_2CO_3 in aq. $COMe_2$ gives p-*arsinoxidobenz-βγ-dihydroxypropylamide*, amorphous, decomp. >250°, with N_2H_4,H_2O in C_5H_5N–C_6H_6 gives s-*di*-p-*arsinoxidobenzoyl-hydrazine*, amorphous, decomp. >360°, and with CN·CH_2·NH_2,H_2SO_4 in Na_2CO_3 gives p-*arsinoxidobenzcyanomethylamide*, amorphous, decomp. >265°, oxidised by I to the *arsonic acid*, m.p. 251—252° (decomp.). Similarly (**VI**) with $(CH_2·NH_2)_2$ or NHAc·NH_2 gives s-*di*-p-*arsinoxidobenzethylenediamide*, amorphous, decomp. >320°, or N-p-*arsinoxidobenzoyl*-N′-*acetethylenediamide*, amorphous, decomp. 270—272° (decomp.), respectively. *Glycylacetanilide*-p-*dichloroarsine hydrochloride* is obtained from the NO_2-compound and is hydrolysed to the AsO-compound. N-p-*Toluoylarsanilic acid* (prep.: Schotten–Baumann), m.p. >360°, with $KMnO_4$–$MgSO_4$–H_2O gives *p*-$C_6H_4(CO_2H)_2$ (100%). *p*-$C_6H_3(COCl)_2$ and *o*-NH_2·C_6H_4·AsO_3H_2 (**VII**) give NN′-*terephthaloyldiarsanilide* (25%), amorphous, decomp. >250°, and p-*arsonoterephthalanilic acid* (5%), m.p. >360° (cf. G.P. 191,548). *p*-CN·C_6H_4·COCl (prep. from the acid by $SOCl_2$ and C_5H_5N in Et_2O) and (**VII**) give N-p-*cyano-*, amorphous, m.p. >360°, converted by 3% H_2O_2 into N-p-*carbamyl-benzoylarsanilic acid*, m.p. >360°, whence the amorphous *arsine oxide*, m.p. 319°, is obtained. *p*-NH_2·C_6H_4·S·C_6H_3·NO_2-*p* gives (Scheller–Bart) p-p′-*nitrophenylthiolphenylarsonic acid* (39%), m.p. 291—292°, and thence the NH_2-acid, decomp. >190°, and (Sandmeyer) the *CN-acid* (32%), decomp. >200°, whence H_2O_2 yields p-p′-*carbamylbenzenesulphonylphenylarsonic acid*, m.p. 310·5°.

VIII. ArN_2Cl couples with *o-* and *m*-OH·C_6H_4·AsO_3H_2 in the position *p-* to OH; when the OH is *p-* to the AsO_3H_2, partial replacement of AsO_3H_2 by ArN_2 and then further coupling occur, the amounts of three reactions depending largely on the pH. The Bart and Schcller–Bart reactions can also be used with azobenzene derivatives. 2-*Hydroxy-5-*, m.p. 257·3°, and *o-hydroxy-2-benzeneazophenylarsonic acid*, m.p. 237·5°, are obtained by coupling in $NaHCO_3$ or NaOH; they are converted by hydrogenation (Raney Ni) and then reduction in HCl into 4-amino-2-, m.p. 183—183·4°, and *5-amino-4-dichloroarsinophenol hydrochloride*, m.p. 128—128·2°, respectively. *p*-OH·C_6H_4·AsO_3H_2 (**VIII**) at pH 5·8—6·6, 7·3—7·4, or 8·5—9·5 (respective yields in parentheses) gives *p*-PhN_2·C_6H_4·OH (36·9, 39·4, 9·4), 4-*hydroxy-3-benzeneazophenylarsonic acid* (0·5, 5·9, 0), m.p. 290° (obtained in 40% yield by a Scheller–Bart reaction), and 2 : 4 : 1-$(PhN_2)_2C_6H_3$·OH (4·6, 12·2, 27·8%). (**VIII**) does not couple with *p*-N_2Cl·C_6H_4·CO_2H or *m*-C_6H_4Mc·N_2Cl. 2 : 4 : 1-$(OH)_2C_6H_3$·AsO_3H_2 at pH 7·6—7·9 or 8·5—9·5 gives 84 and 5·6%, respectively, of 2 : 4-*dihydroxy-3* : 5-*dibenzeneazophenylarsonic acid*, m.p. 268°, with, in the latter case, mixed phenols. 4 : 1-OH·$C_{10}H_5$·AsO_3H_2 (**IX**) at pH 7·1—7·4 gives 4 : 1-PhN_2·$C_{10}H_4$·OH (34·4%), $(PhN_2)_2C_{10}H_5$·OH (33·8%), and 4-*hydroxy-1-benzeneazonaphthylarsonic acid* (**X**) (20%), m.p. 245°. 4-*Amino-1-naphthyl benzoate* (prep. from the NO_2-ester by H_2–Raney Ni in EtOH or from the NH_2-ester hydrochloride by NH_3), m.p. 107·2—107·6°, gives (Scheller–Bart) 4-*arsono-1-naphthyl benzoate* (19%), m.p. 199·8—200°, whence cold HCl–MeOH yields (**IX**) (57%) and MeOBz. H_2–Raney Ni reduces the Na_1 salt of (**X**) to 2-*amino-1-naphthol-4-arsonic acid*, decomp. when heated, whence 4-*hydroxy-1* : 4-*α-naphth*-isooxazine-6-*arsonic acid* is prepared. Bart, or, better, Bart–Scheller, reactions yield *p*-PhN_2·C_6H_4·AsO_3H_2, m.p. 332·5—333·5°, p-*toluene*-p′-*azophenyl-* (**XI**), m.p. >360°, and 4-*hydroxy-3-benzeneazophenyl-arsonic acid*, but failed with p-5-*amino-2-hydroxyazobenzene-4′-sulphonic acid* (*Na* salt of the Ac derivative) and its *amide* (*Ac* derivative). Oxidising (**XI**) by $KMnO_4$ gives p-p′-*arsonobenzeneazobenzoic acid*, m.p. >360°, converted by PCl_5–$POCl_3$ and then aq. NH_3 R into p-p′-*arsinoxidobenzeneazobenz-amide*, decomp. >260°, and *-β-hydroxyethylamide*, decomp. >275°.
p-AsO_3H_2·C_6H_4·N_2Cl and *o*-NHAc·C_6H_4·OH give p-3′-*acetamido-*, m.p. 224·8—225·2°, and thence (HCl–MeOH) p-3′-*amino-4′-hydroxybenzeneazophenylarsonic acid*, decomp. when heated. R. S. C.

Mercuripurine derivatives of phthalimide. G. Carrara and E. Mori (*Gazzetta*, 1943, **73**, 113—116).—Allylphthalimide [new prep. from $C_6H_4(CO)_2O$ and allylamine] and $Hg(OAc)_2$ in MeOH at the b.p. give N-*β-acetatomercuri-γ-methoxypropylphthalimide*, m.p. 139—140°, which with theophylline gives *α-phthalimido-γ-methoxy-β-propylmercuritheophylline*, m.p. 225—226°. E. W. W.

IX.—PROTEINS.

Stromctin.—See A., 1944, III, 450.

X.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Formation of " excess material " in the treatment of wood with sodium chlorite and its significance for the chemistry of wood and lignin. G. Jayme, L. Eser, and G. Hanke (*Naturwiss.*, 1943, **31**, 275—276).—Subjection of the solutions obtained by treating wood with $NaClO_2$ to dialysis and electrodialysis yields from pine 10·13% of material with 8·62% OMe and 22·30% lignin residue and from poplar 9·42% of material with 6·84% OMe and 25·05% lignin residue. In these cases the excess material amounts to 7·87% and 7·06% respectively; this consists of a mixture of substances with short chains the individual fractions of which give varying amounts of residue in the customary lignin determination. The observations are explained by assuming the presence of a polysaccharide of the hexose type or its precursor substituted mainly with guaiacyl residues, two aromatic residues being united to each pyranose ring by the loss of 1·5—2 mols. of H_2O or 0·5—2 atoms of O. H. W.

Isolation of euphol and α-euphorbol from euphorbium. G. T. Newbold and F. S. Spring (*J.C.S.*, 1934, 249—252).—Two cryst. monohydric alcohols have been isolated by the chromatographic method from euphorbone, an amorphous solid obtained from euphorbium. One of these is identical with α-euphorbol (cf. Bauer *et al.*, A., 1931, 847), m.p. 126—127°, $[\alpha]_D^{17}$ ±0° in $CHCl_3$ [*acetate*, m.p. 124—125°, $[\alpha]_D^{15}$ ±0° in $CHCl_3$; *benzoate*, m.p. 133—135°, $[\alpha]_D$ + 15° in C_5H_5N; *acetate dibromide*, m.p. 169—171° (decomp.)], which contains at least two double bonds, the acetate being reduced to *dihydro-α-euphorbyl acetate*, m.p. 133—135°, $[\alpha]_D^1$ −15° in C_5H_5N. The second component is *euphol*, $C_{30}H_{50}O$ (?), m.p. 116°, $[\alpha]_D^{19·5}$ +32° in $CHCl_3$, containing two double bonds, one of which is relatively inert; it gives an *acetate*, m.p. 109°, $[\alpha]_D^2$ +41° in $CHCl_3$, *benzoate*, m.p. 137—139°, $[\alpha]_D^{18·5}$ +59° in C_5H_5N, *acetate dibromide*, m.p. 138·5—139·5°, $[\alpha]_D^{20}$ +23·5° in $CHCl_3$, and *dihydroeuphol*, m.p. 120°, $[\alpha]_D^{18·5}$ +34° in $CHCl_3$ (*acetate*, m.p. 123·5—124°, $[\alpha]_D^{19}$ +34·5° in $CHCl_3$, and *benzoate*, m.p. 160—161°). F. R. S.

Biochemistry of *Eidamella spinosa*.—See A., 1944, III, 502.

Folic acid. I. Concentration from spinach. H. K. Mitchell, E. E. Snell, and R. J. Williams. **II. Adsorption.** E. H. Frieden, H. K. Mitchell, and R. J. Williams. **III. Chemical and physiological properties.** H. K. Mitchell and R. J. Williams. **IV. Absorption spectra.** H. K. Mitchell (*J. Amer. Chem. Soc.*, 1944, **66**, 267—268, 269—271, 271—274, 274—278; cf. A., 1941, III, 1066).—I. The filtrate obtained from pulped spinach (1000 lb.) by H_2O at 30—35° and then the b.p. is adjusted to pH 3·0—3·2, treated with " Super-cel," filtered, and stirred with C. The C is eluted with boiling 2·55% aq. NH_3, which is then stirred with C pretreated with aq. NH_2Ph and then H_2O. Elution by boiling 8% aq. NH_2Ph, extraction with Et_2O, and adjustment of pH to 3·0—3·2 are then followed by a similar adsorption and elution. Finally follow successive pptn. by $Pb(OAc)_2$, elution of the ppt. by boiling aq. $(NH_4)_2SO_4$, pptn. by aq. $AgNO_3$ at pH 6·5, elution by boiling aq. NH_4Cl, pptn. by Lloyd's reagent, elution by 5% aq. NH_3, adsorption on Al_2O_3, fractional elution by NH_3–MeOH–H_2O, pptn. by HCl at 0°, redissolution in aq. NH_3, adsorption on Al_2O_3, and elution and pptn. as above. Thus are obtained 1·2 mg. of amorphous folic acid (I) having a potency 137,000 times as great as Wilson liver fraction *B* when tested as growth stimulant for *Streptococcus lactis R*. Other procedures are less effective.

II. Impure (I) is readily eluted from C on which it has been adsorbed, but pure (I) is tenaciously retained. Retention of pure (I) is rendered less severe by pretreatment of the C by adsorbable substances. Adsorption isotherms confirm the dual nature of the adsorption; equilibrium is reached only slowly. Similar isotherms for riboflavin and thiochrome on C indicate similar phenomena.

III. (I) is readily inactivated by oxidation, reduction, acid, alkali, dry heat, light, acylation, esterification, methylation, benzylation, HNO_2, NaOBr, Br, etc., but the mol. wt. and absorption spectra (and thus chemical structure) are often little affected by these changes. The mol. wt., determined by diffusion, and analyses indicate $C_{15}H_{15}O_8N_5$ as approx. formula. (I) is required for the growth of 4 yeasts, but the relative amounts of different concentrates required for yeasts and bacteria may vary. Thymine (1 μg. per ml.) may replace (I) for *S. lactis R*, as also may 10 μg. per ml. of 9 other pyrimidine derivatives, but numerous other compounds are ineffective. (I), having potency 75,000, has one fifth of the anti-anæmia activity of xanthopterin (II).

IV. Absorption spectra and the effect of pH thereon are very similar for (I) and (II), indicating a similar structure. Results are recorded also for other pyrimidine derivatives. Purification affects the spectra, but inactivation has much less effect. For (I), (II), etc. sudden changes in adsorption at pH ~2·5 and ~9 are due to electronic shifts and tautomerism, respectively. R. S. C.

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A II—Organic Chemistry.

SEPTEMBER, 1944.

I.—ALIPHATIC.

Reactions of hydrocarbons with sulphuryl chloride and with sulphur dioxide–chlorine mixtures.—See A., 1944, I, 206.

α-Methylenic reactivity in olefinic systems. I. Prins reaction with propylene. J. W. Baker (*J.C.S.*, 1944, 296—301).—$CHMe{:}CH_2$ with paraformaldehyde in 100% AcOH—100% H_2SO_4 at 35° gives the *diacetate* (**I**), b.p. 65°/1 mm., of $OH{\cdot}CHMe{\cdot}[CH_2]_2{\cdot}OH$ (**II**) (63·5%) (*di-α-naphthylurethane*, m.p. 153°), *4-methyl-1 : 3-dioxan* (**III**) (14%), b.p. 25°/22 mm., and *4-acetoxytetrahydro-γ-pyran* (**IV**) (22·5%), b.p. 47·5°/1 mm. (**III**) with 2 : 4 : 1-$(NO_2)_2C_6H_3{\cdot}NH{\cdot}NH_2$ in aq. HCl yields the hydrazone of CH_2O and (**II**). (**IV**) is hydrolysed [aq. $Ba(OH)_2$] to *4-hydroxytetrahydro-γ-pyran* (**V**), b.p. 60·5°/0·7 mm. (*p-nitrobenzoate*, m.p. 69°), oxidised (CrO_3) to tetrahydro-4-pyrone (**VI**), b.p. 73°/20 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 186—187°). Oxidation (HNO_3) of (**IV**), (**V**), and (**VI**) affords $CO_2H{\cdot}CH_2{\cdot}O{\cdot}[CH_2]_2{\cdot}CO_2H$, m.p. 97° [*diamide*, m.p. 174°; *Me*$_2$ ester, b.p. 138°/24 mm.; *Me ester amide* (?), m.p. 73°], reduced by HI to $I{\cdot}[CH_2]_2{\cdot}CO_2H$. (**II**) with CH_2O in $AcOH–H_2SO_4$ gives (**I**) and (**III**) but no (**IV**). Results for a kinetic examination are given, and it is suggested that (**II**) and (**III**) are formed by acid-catalysed addition of CH_2O to the double linking but (**IV**) is obtained by reaction with H of Me of $CHMe{:}CH_2$ activated by conjugation. BF_3 does not catalyse the Prins reaction, but improves the catalytic efficiency of H_2SO_4. D. G.

Production of α- and β-pyronene from *allo*ocimene. L. A. Goldblatt and S. Palkin (*J. Amer. Chem. Soc.*, 1944, **66**, 655—656).—Pyrolysis (apparatus : C, 1944, Part 4) of *allo*ocimene at, best, 400° gives α- (~30%), b.p. 54—56°/20 mm., and β-pyronene (~45%), b.p. 62—64°/20 mm. R. S. C.

Conjugated systems. XXIII. Synthesis and properties of dihalogeno-derivatives of isoprene. A. A. Petrov (*J. Gen. Chem. Russ.*, 1943, **13**, 331—338).—$OH{\cdot}CMe_2{\cdot}C{:}CH$ (**I**), in cold $CHCl_3$, with 0·75 mol. of Cl_2, yields polychloro-derivatives and 50% of $OH{\cdot}CMe_2{\cdot}CX{:}CHX$ (**II**), X = Cl, *trans*-form, b.p. 61·5—62°/10 mm.; dehydration of the latter by P_2O_5, with short time of contact, gives 35% of *αβ-dichloro-γ-methyl-*$\Delta^{\alpha\gamma}$*-butadiene* (**III**), b.p. 60·5—61°/85 mm., and a yellow, powdery polymer. Bromination of (**I**) (accelerated by illumination), under similar conditions, yields 95% of *γδ-dibromo-β-methyl-*Δ^{γ}*-buten-β-ol*, [(**II**), X = Br], b.p. 91·5—92·5°/10 mm.; a higher-boiling form of (**II**), X = Br, was obtained, in one isolated experiment, together with the product described. (**II**), X = Br, is dehydrated over P_2O_5 at 100°/20 mm. to a mixture of cis- and trans-*αβ-dibromo-γ-methyl-*$\Delta^{\alpha\gamma}$*-butadiene*, b.p. 51·5—52°/10 mm. (**IV**) (probably *trans*-) and b.p. 66·5—67°/10 mm. (**V**). (**III**) and (**IV**), in PhMe at 100°, form sticky polymers (7—8% in 1 hr.) and, on keeping in diffused light, become viscous in 4—5 months owing to formation of soft rubber-like polymers; they do not condense with $(CH{\cdot}CO)_2O$. In boiling 20% KOH–EtOH, (**III**), (**IV**), and (**V**) react in 30 min. to the extent of 8, 25, and 44% respectively, (**IV**) and (**V**) yielding $CH_2{:}CMe{\cdot}C{\cdot}CBr$. (**II**), X = Cl or Br, is decomposed by alcoholic or aq. KOH to $COMe_2$, $CHX{:}CHX$, and $CH{:}CX$; *trans*-(**II**), X = Cl, yields *trans*-$C_2H_2X_2$. R. C. P.

Conjugated systems. XXIV. Reaction of isoprene with hypobromous acid and with alkyl hypoiodites. A. A. Petrov (*J. Gen. Chem. Russ.*, 1943, **13**, 481—490).—HOBr, as NHAcBr (**I**), and isoprene (**II**) (1 : 1·5 mol.) give *δ-bromo-γ-hydroxy-γ-methyl-*Δ^{α}*-butene* (**III**), b.p. 49·5°/10 mm. (33% yield on HOBr), an *isoprene dibromide*, m.p. 86° (yield <25%), besides oily dibromides and products of reaction of (**II**) with (**I**) itself. (**III**) affords with AcCl a *monoacetate* (**IV**), with Cl-compounds, whilst with Ac_2O it gives 91% pure (?) (**IV**), b.p. 60°—95°. Br and (**III**) give *αβδ-tribromo-γ-hydroxy-γ-methylbutane*, b.p. 136·5°/10 mm., which is largely unchanged on treatment with $Na_2Cr_2O_7$ in $AcOH–H_2SO_4$, but with aq. 80% KOH at 120° it gives *αβ*-epoxy-*β*-methyl-Δ^{γ}-butene (70% yield), b.p. 78·5—79°/715 mm., decomposed by H_2SO_4 to tiglaldehyde. Treatment of (**I**) with (**II**) (2 : 1 mol.) gives *αγ-dibromo-βγ-dihydroxy-β-methylbutane*, m.p. 86°. (**II**) with HgO, I, and either MeOH or EtOH gives *δ-iodo-γ-methoxy-*, b.p. 60°/10 mm., or *δ-iodo-γ-ethoxy-*, b.p. 66·5°/10 mm., *-γ-methyl-*Δ^{α}*-butene*. F. Hi.

Preparation and purification of glucose 1-phosphate with the aid of ion exchange adsorbents. R. M. McCready and W. Z. Hassid (*J. Amer. Chem. Soc.*, 1944, **66**, 650—563).—Potato starch is digested with crude potato phosphorylase in presence of Na phosphates, inorg. phosphates are then removed by $Mg(OAc)_2–NH_3$, and the filtrate is passed through a cation-absorbing resin, Amberlite IR-100. The resulting acid solution is then passed through an anion-absorbing resin, Amberlite IR-4; weak acids pass through but glucose-1-phosphoric acid is adsorbed and subsequently recovered by aq. NH_3 and pptn. as K$_2$ salt, $+2H_2O$, $[\alpha]_D$ +78° in H_2O. Glucose-6-, fructose-6-, and glycero-phosphoric and fructose-1 : 6-diphosphoric acids are similarly purified. R. S. C.

Carboxonium salts. I. Acetyl fluoborate. F. Seel (*Z. anorg. Chem.*, 1943, **250**, 331—351).—*Acetyl fluoborate*, $Ac[BF_4]$ (**I**), obtained as white crystals by direct union of AcF and BF_3, dissociates appreciably at room temp. and completely at the b.p. of AcF. It is hydrolysed by H_2O to AcOH and HBF_4. With dry KF it affords AcF and KBF_4; with other K halides in presence of ionising solvents (*e.g.*, liquid SO_2) it gives KBF_4 and Ac halide. With $NaNO_2$ it reacts : $NaNO_2 + 2(I) \rightarrow NaBF_4 + (NO)BF_4 + Ac_2O$. EtOH and AcOH give EtOAc and Ac_2O respectively. $NO{\cdot}OEt$ affords $NO{\cdot}BF_4$ and EtOAc. Warm Et_2O yields AcF and $BF_3{,}Et_2O$, which when further heated form EtOAc, BF_3, and EtF. (**I**) is an electrolyte in liquid SO_2, *A* at −70° being approx. that of KI, but decreasing rapidly with rising temp. Its reactions with KI and KOAc may be followed conductometrically. Its structure is ionic, $[Ac]^+[BF_4]^-$. F. J. G.

Allylic rearrangements. XV. Carbonation of magnesium butenyl bromide. J. F. Lane, J. D. Roberts, and W. G. Young (*J. Amer. Chem. Soc.*, 1944, **66**, 543—545; cf. A., 1944, I, 157).—Adding the Grignard solution from mixed $CHMe{:}CH{\cdot}CH_2Br$ (80%) + $CH_2{:}CH{\cdot}CHMeBr$ (20%) to solid CO_2 gives 75% of $CH_2{:}CH{\cdot}CHMe{\cdot}CO_2H$ (**I**), b.p. 95·5°/35 mm. (chloride, b.p. 55—58°/110 mm.; amide, m.p. 98°, hydrogenated to $CHMeEt{\cdot}CO{\cdot}NH_2$; *CHPhMe·NH*$_2$ salt, m.p. 119·5—120·5°). Arnold's method (A., 1942, II, 142) gives 63% of (**I**), 13% of *dibutenyl ketone*, b.p. 93—94°/100 mm., smaller amounts of octadienes, b.p. 52—53°/100 mm., and a fraction, b.p. 100—115°/30 mm. R. S. C.

Reduction of ester vinylogues. R. H. Baker and P. C. Weiss (*J. Amer. Chem. Soc.*, 1944, **66**, 343—345).—2-Ethylchromone is unaffected by boiling $Al(OPr^{\beta})_3$–$Pr^{\beta}OH$, as also is $CHBz{:}CMe{\cdot}OEt$ (**I**), which is largely unchanged by $Al(OBu\text{-}sec.)_3$ at 100°; $OEt{\cdot}CH{:}CAc{\cdot}CO_2Et$ (**II**) gives a (polymerised) tar with a little dimeride. With H_2–Raney Ni, (**II**) at 23° gives $CHMeAc{\cdot}CO_2Et$ (50%), (**I**) at 118° gives $OEt{\cdot}CHMe{\cdot}CH_2{\cdot}CHPh{\cdot}OH$ (**III**) (57%) and at 120° gives, after absorption of only 1 H_2, 64% of (**III**) + $CH_2Bz{\cdot}CHMe{\cdot}OEt$; $OEt{\cdot}CMe{:}CH{\cdot}CO_2Et$ (**IV**) at 130° gives $OEt{\cdot}CHMe{\cdot}CH_2{\cdot}CO_2Et$ (**V**) (86%). With H_2–Cu chromite, (**II**) at 150° gives a tar, (**I**) at 180° gives $COPhPr^{\alpha}$ (58%), and (**IV**) at 170° gives (**V**) (45%). R. S. C.

Autoxidation of β-elæostearic acid. Application of the spectrophotometer to the study of the course and the kinetics of the reaction.—See A., 1944, I, 204.

Cryoscopy [and structure] of isanic acid.—See A., 1944, I, 169.

β-Lactones and β-lactonic acids. III. Condensation of citral with malonic acid. N. S. Vulfson and M. M. Schemjakin (*J. Gen. Chem. Russ.*, 1943, **13**, 436—447).—Citral with $CH_2(CO_2H)_2$ in presence of piperidine and AcOH affords, via $CMe_2{:}CH{\cdot}[CH_2]_2{\cdot}CMe{:}CH{\cdot}CH{:}C(CO_2H)_2$ (**I**), both $CMe_2{:}CH{\cdot}[CH_2]_2{\cdot}CMe{:}CH{\cdot}CH{:}CH{\cdot}CO_2H$, b.p. ~170°/15 mm., and the *βδ-dilactone* of (**I**), viz., $CMe_2{:}CH{\cdot}[CH_2]_2{\cdot}CMe{\cdot}CH_2{\cdot}CH{\cdot}CH{\cdot}CO$ (**II**), m.p. 187°. When titrated with aq. NaOH (**II**) behaves as a monobasic acid : with boiling aq. NaOH both rings open and on acidification the product affords the corresponding *δ-hydroxy-β-lactonic acid*, m.p. 113—114° (**III**), with the δ-hydroxy-β-lactone, m.p. 119·5—120·5° (**IV**). With boiling AcCl (**III**) gives (**II**), CO_2, (**IV**), and the *monoacetate* (**V**) of (**IV**) (?), whilst on long heating with H_2O or with C_5H_5 (**IV**) is formed. Oxidation of (**III**) by aq. $KMnO_4$ in alkaline solution gives $H_2C_2O_4$ but no HCO_2H; hence the lactone ring is formed at the β-position. (**IV**) is unattacked by boiling Ac_2O;

thus the OH is on a *tert.* C so that it is a δ-lactone; with AcCl it gives (**V**), m.p. 117—118°. F. Hi.

β-Lactones and β-lactonic acids. IV. Rate of fission of the β-lactone ring.—See A., 1944, I, 204.

Action of aromatic diazo-compounds on alkylacetoacetic esters as a method of preparing arylhydrazones of α-keto- and α-amino-acids. VII. Synthesis of *n*-valine. V. V. Feofilaktov and V. N. Zaitzeva (*J. Gen. Chem. Russ.*, 1943, **13**, 358—362).—CHPrAc·CO_2Et (**I**) and PhN_2·OK, under conditions already specified (A., 1940, II, 70, 85), give NHPh·N:CPr·CO_2Et (**II**) (35·4%) in a *form*, m.p. 103°, not previously described; reduction of (**II**) by Zn dust and HCl–EtOH, followed by treatment with Ag_2CO_3 and H_2S, yield *n*-valine (**III**) (77·4%). Similarly, (**I**) and *p*-$C_6H_4Me·N_2·OK$ give a mixture of two forms of *α-ketovaleric acid* p-*tolylhydrazone* (**IV**) (43·5%); crystallisation from C_6H_6 yielded the α-form, m.p. 134—135°, and an inseparable mixture of the α- and β-forms, m.p. 123—131°. Reduction of (**IV**) (α- and β-forms mixed) as above gives (**III**) (96·4%). R. C. P.

Action of aromatic diazo-compounds on substances of the type of alkylacetoacetic esters as a method for obtaining arylhydrazones of α-keto-acids and of α-amino-acids. IX. Reaction of ethyl *cyclo*hexan-2-onecarboxylate with diazobenzene. V. V. Feofilaktov and A. Ivanov (*J. Gen. Chem. Russ.*, 1943, **13**, 457—467).—The reaction of cyclic compounds allied to monoalkylacetoacetic esters with aromatic diazo-compounds has been studied partly to widen the scope of the method of obtaining α-NH_2-acids from monoalkylacetoacetic esters and partly to obtain α-aminodicarboxylic acids. Et *cyclo*hexan-2-one-1-carboxylate with PhN_2Cl in acid aq. EtOH containing NaOAc affords $CO_2H·[CH_2]_3·C(:N·NHPh)·CO_2Et$ in 98% yield, the product beng an *α-form*, m.p. 89·5—90°, admixed with a minor proportion of a β-form (cf. Jackson and Manske, A., 1931, 363); hydrolysis of the mixture gives α-ketopimelic acid phenylhydrazone in two forms; that predominating (**I**) (from α-ester ?) has m.p. 143—144°; the other form has m.p. 131—132° (cf. Linstead and Wang, A., 1937, II, 340). With HCl in aq. EtOH and Zn dust (**I**) gives $CO_2H·[CH_2]_3·CH(NH_2)·CO_2H$. F. Hi.

Thermal decomposition of acetaldehyde.—See A., 1944, I, 204.

Preparation of ketones from nitro-olefines. (Miss) D. Nightingale and J. R. Janes (*J. Amer. Chem. Soc.*, 1944, **66**, 352—354).—AlkCHO and $CH_2Alk'·NO_2$ give 70—80% of OH·CHAlk·CHAlk'·NO_2, the acetate of which with boiling $NaHCO_3$–MeOH–H_2O gives 90—95% of CHAlk:CAlk'·NO_2, decomposed at the b.p./1 atm., reduced by Zn dust in boiling Et_2O–25% AcOH to $CH_2Alk·CAlk':N·OH$ (usually 50—60%), whence boiling CH_2O–H_2O–H_2SO_4 yields $COAlk'·CH_2Alk$. The following are described, m.p. in parentheses being those of the *α-naphthylurethanes*. α-, b.p. 75°/2 mm. (m.p. 118—119°), and *γ-nitrobutan-β-ol*, b.p. 78°/17 mm. (m.p. 122—123°); α-, b.p. 85°/2 mm. (m.p. 99—100°), and *γ-nitropentan-β-ol*, b.p. 78°/2 mm; (m.p. 100—101°); *β-nitropentan-γ-ol*, b.p. 79°/2 mm. (m.p. 126°). γ-, b.p. 64°/2 mm. (m.p. 137°), and *α-nitro-γ-methylbutan-β-ol*, b.p. 66°/1 mm. (m.p. 97·5—98°); *α-nitrohexan-β-ol*, b.p. 80°/1 mm. (m.p. 103°); *β-nitrohexan-γ-ol*, b.p. 82°/2 mm. (m.p. 136—137°); *γ-nitrohexan-δ-ol*, b.p. 89°/2 mm. (m.p. 113—114°); *β-nitro-*δ-, b.p. 89°/2 mm. (m.p. 112—113°), and *-β-methylpentan-γ-ol*, b.p. 75°/4 mm. (m.p. 97—98°); *α-nitroheptan-β-ol*, b.p. 105°/2 mm.; *β-nitroheptan-γ-ol*, b.p. 92°/2 mm.; *γ-nitroheptan-δ-ol*, b.p. 92°/2 mm.; *α-nitro-γ-ethyl-pentan-β-ol*, b.p. 93°/2 mm., and *-heptan-β-ol*, b.p. 110°/2 mm.; *γ-nitro-ε-methylhexan-γ-ol*, b.p. 78°/2 mm.; *β-nitro-β-methylhexan-γ-ol*, b.p. 81°/2 mm., and *-δ-ethylhexan-γ-ol*, b.p. 92°/2 mm.; *γ-nitro-γ-ethylheptan-δ-ol*, b.p. 87°/2 mm.; *β-nitro-octan-γ-ol*, b.p. 85°/2 mm.; *γ-nitro-octan-δ-ol*, b.p. 94°/2 mm., *-nonan-δ-ol*, b.p. 108°/2 mm., and *-decan-δ-ol*, b.p. 108°/2 mm.; *β-nitro-δ-ethyloctan-γ-ol*, b.p. 102°/2 mm.; *γ-nitro-ε-ethyloctan-δ-ol*, b.p. 100°/2 mm.; *β-nitro-*Δ^{β}*-hexene*, b.p. 53°/1 mm., *-δ-methyl-*Δ^{β}*-pentene*, b.p. 57°/1 mm., and *-δ-ethyl-*Δ^{β}*-hexene*, b.p. 84°/1 mm.; *γ-nitro-*Δ^{γ}*-hexene*, b.p. 53°/1 mm., *-ε-methyl-*Δ^{γ}*-hexene*, b.p. 53°/1 mm., *-ε-ethyl-*Δ^{γ}*-heptene*, b.p. 65°/1 mm., *-*Δ^{γ}*-decene*, b.p. 97°/1 mm., *-δ-ethyl-*Δ^{β}*-octene*, b.p. 84°/1 mm., and *-ε-ethyl-*Δ^{γ}*-octene*, b.p. 94°/1 mm.; *α-nitro-*Δ^{α}*-heptene*, b.p. 57°/1 mm.; *γ-oximino-ε-ethylheptane*, b.p. 75—79°/1 mm., *-decane*, b.p. 81°/1 mm., *-heptane*, b.p. 56°/1 mm., *-nonane*, b.p. 70°/1 mm., *-ε-ethylnonane*, b.p. 89—92°/1 mm., and *-ε-methylhexane*, b.p. 55°/1 mm.; *β-oximino-δ-ethylhexane*, b.bp. 69°/1 mm., and *-δ-ethyloctane*, b.p. 81°/1 mm.; *ε-ethylnonan-γ-one*, b.p. 53°/1 mm. Efforts to condense the nitro-olefines with $(CH_2:CH)_2$ or *cyclo*pentadiene failed. R. S. C.

Condensation of *iso*butaldehyde with aliphatic ketones. S. G. Powell and F. Hagemann (*J. Amer. Chem. Soc.*, 1944, **66**, 372—376).—PrβCHO with COMeR (R = Prα, Buα, Buβ, *n*-amyl, or *n*-hexyl) in KOH–EtOH at <35° gives 35—65% of CHPrβ:CH·COR (*A*); only *n*-C_5H_{11}·COMe gives a little CHPrα:CBuα·COMe (*hydantoin* derivative, m.p. 175—176°). Na in $NaHCO_3$–Et_2O–H_2O usually converts (*A*) into CHPrβ:CH·CHR·OH, but reduction is sometimes incomplete; H_2–PtO_2 is always effective. *β-Methyl-*Δ^{γ}*-n-decen-ε-one*, b.p. 223—224° (*hydantoin* derivative, m.p. 135—136°), with Na–EtOH gives *β-methyl-*Δ^{β}*-n-decen-ε-ol* (42%), b.p. 129·5—131°/30 mm. (3 : 5-dinitrobenzoate, an oil), whence O_3 gives $COMe_2$ (no PrβCHO) and Δ^{α}-octenaldehyde [semicarbazone, m.p. 169—170° (lit. 163°)]. $COEt_2$ and PrβCHO give CHPrβ:CMe·COEt, b.p. 176—178° (2 : 4-dinitrophenylhydrazone, m.p. 174—175°) (cf. Franke *et al.*, A., 1924, i, 6). The following are described: m.p. prefixed by *h* are those of the derived *hydantoins*. CHPrβ:CH·COPrα, b.p. 85—86°/25 mm.; *β-methyl-*Δ^{γ}*-n-nonen-ε-one*, b.p. 103—105°/25 mm. (*h* m.p. 149·5—150°); *βη-dimethyl-*Δ^{ϵ}*-n-octen-δ-one*, b.p. 199—200°; *β-methyl-*Δ^{γ}*-n-undecen-ε-one*, b.p. 135—136°/28 mm. (*h* m.p. 118·5—119°); COPrα·CH_2Buβ, b.p. 177—179° [semicarbazone, m.p. 144·5—145·5° (cf. lit.); *h* m.p. 175—175·5°]; *β-methyl-n-nonan-ε-one*, b.p. 203—204° (*h* m.p. 192—192·5°); *βη-dimethyl-n-octan-δ-one*, b.p. 196—198° (semicarbazone, m.p. 78—79°; *h* m.p. 216—217°); *β-methyl-n-decan-ε-one*, b.p. 119—121°/28 mm. [*nitroguanylhydrazone*, m.p. 78—79·5° (decomp.); *h* m.p. 192—192·5°]; *β-methyl-n-undecan-ε-one*, b.p. 126—128°/23·5 mm. [*nitroguanylhydrazone*, m.p. 84·5—86° (decomp.); *h* m.p. 175—175·5°]; *δζ-dimethyl-n-heptan-γ-one*, b.p. 170—173° (*h* m.p. 186—186·5°); *β-methyl-n-nonan-ε-ol*, b.p. 111·5—113°/28·5 mm. (3 : 5-*dinitrobenzoate*, m.p. 63·5—64·5°); $CH_2Bu^{\beta}·CHBu^{\beta}·OH$, b.p. 107—108°/29·5 mm. (3 : 5-*dinitrobenzoate*, m.p. 81—82°); *β-methyl-n-decan-ε-ol*, b.p. 122·5—123°/24 mm. (124—126°/24 mm.); *β-methyl-n-undecan-ε-ol*, b.p. 132—133°/24 mm. (135°/24 mm.). M.p. and b.p. are corr. R. S. C.

Synthesis of bromoacetals. P. Z. Bedoukian (*J. Amer. Chem. Soc.*, 1944, **66**, 651—652).—Adding Br to CH_2:CH·OAc in CCl_4 at 0—10° and pouring the mixture into ROH gives bromoacetaldehyde Me_2 (80—85%), b.p. 48—49°/14 mm., and Et_2 acetal (75—80%), b.p. 64—65°/16 mm. R. S. C.

Anomalous base strength of the methylamines.—See A., 1944, I, 175.

Geranylamine. D. A. Sutton (*J.C.S.*, 1944, 306).—Geranylamine hydrochloride, m.p. 145—146° (modified prep.), is a single substance, CMe_2:CH·$[CH_2]_2$·CMe:CH·$CH_2·NH_3Cl$. F. R. S.

Solubilities of symmetrical, normal aliphatic secondary amines of high mol. wt. C. W. Huerr, H. J. Harwood, and A. W. Ralston (*J. Org. Chem.*, 1944, **9**, 201—210).—The solubilities of dioctylamine, m.p. (α form) 14·60°, (β-form) 26·7° (lit. 36·5 and 34° respectively), f.p. 14·60°, didodecylamine, m.p. (α-form) 46·9° (lit. 51—53°), β-form 51·8°, f.p. 46·9°, *ditridecylamine*, m.p. 56·5°, f.p. 56·5°, ditetradecylamine, m.p. 60·6° (lit. 56—58°), f.p. 60·6°, *dipentadecylamine*, m.p. 63·3°, f.p. 63·3°, and dioctadecylamine, m.p. 72·3° (lit. 71—72°), f.p. 72·3°, have been determined in C_6H_6, *cyclo*hexane, CCl_4, $CHCl_3$, Et_2O, EtOAc, BuOAc, $COMe_2$, COMeEt, MeOH, 95% EtOH, PrβOH, BuαOH, and MeCN. In general, the *sec.* amines are more sol. in org. solvents than are primary amines of corresponding chain length. This behaviour is apparently due to the fact that the polar group in the centre of the paraffin chain causes the m.p. of the *sec.* amines to be considerably < those of the primary amines containing the same no. of C atoms. If a temp. correction is made for the difference in m.p., the solubility curve of any *sec.* amine can be nearly superimposed on that of the primary amine of equal chain length in any given solvent. Compared in this manner, the *sec.* amines tend to be slightly more sol. in non-polar solvents and somewhat less sol. in the highly polar solvents than the corresponding primary amines. The solubilities of the nitriles, primary and *sec.* amines, which have relatively weak polar groups, tend to suggest that the shapes of the solubility curves are probably due primarily to association of the paraffin chains with the possibility that the more polar compounds such as the acids and amides may be further associated at the polar groups. The *sec.* amines are obtained by heating the respective primary amines with Raney Ni at 200°. H. W.

Metabolism of phosphorylcholine. I. Synthesis of calcium phosphorylcholine chloride containing the radioactive isotope, ^{32}P. R. F. Riley (*J. Amer. Chem. Soc.*, 1944, **66**, 512—513).—Heating choline chloride (**I**) with P_2O_5 and 100% H_3PO_4 containing some ^{32}P at 165°/vac. and treating the product in H_2O with $CaCl_2$ and then $Ca(OH)_2$ to neutrality gives 63% of *Ca phosphorylcholine chloride* (**II**), $C_5H_{13}O_4NClPCa,4H_2O$, containing 96% of the original radioactivity. 24% of (**II**) is obtained by heating choline hydroxide [prep. from aq. (**I**) by, successively, Ag_2CO_3, $Ba(OH)_2$, and evaporation in vac. (N_2)] with H_3PO_4 in PhMe with removal of H_2O and treating the product in aq. EtOH with $CaCl_2$–$Ca(OH)_2$ as above. Ag_3PO_4 or Ag_2PhPO_4 with bromocholine bromide in boiling EtOH gives 65 and 89%, respectively, of neurine. *Phosphorylcholine reineckate* and *phosphotungstate*, the $HgCl_2$ additive *compound* of phosphorylcholine, $C_5H_{15}O_4NP,3HgCl_2$, m.p. 180—184° (corr.), *dicholine phosphate reineckate*, and the additive *compound*, m.p. 202—207°, of dicholine phosphate and $HgCl_2$ are prepared. C

Nitric ester of choline perchlorate, m.p. 188—189°.—See A., 1944, III, 553.

Chromammines. III. Preparation of diacidodiethylenediaminosalts by thermal decomposition of triethylenediamine luteo-salts.—See A., 1944, I, 206.

Spectroscopic evidence for the N·H·N linking in ethyleneimine. H. W. Thompson and G. P. Harris (*J.C.S.*, 1944, 301—303).—Variation in the intensity of an absorption band at 3·1 μ. with the concn. of ethyleneimine in solution in CCl_4 suggests association through N·H·N linkings. Other evidence is adduced in support. D. G.

Polymerisation of ethyleneimine. G. D. Jones, A. Langsjoen, M. M. C. Neumann, and J. Zomlefer (*J. Org. Chem.*, 1944, **9**, 125—147).—The polymerisation of ethyleneimine (**I**) is indicated to involve a bimol. reaction between (**I**) and ethyleneimonium or substituted ethyleneimonium ions. Dimeric (**I**) is identical with *N-β-(aminoethyl)ethyleneimine* (**II**), which appears to be an intermediate in the polymerisation of (**I**). Polyethyleneimine is regarded as a linear poly*sec.*-amine of mean degree of polymerisation 25—100. The polymerisation of (**I**) is not greatly accelerated by ascaridole at 40° or 150°, Bz_2O_2 at 40°, old MeCHO at 40° or 150°, 30% H_2O_2 at 40°, $K_2S_2O_8$ at 40°, $CuSO_4$ at 40°, Cu-bronze, 5N-NaOH at 25°, Bu^{t}Cl, *o-*, *m-*, and *p*-$C_6H_4Cl{\cdot}NO_2$. Some acceleration is caused by 30% H_2O_2 at 145°, and by H_2O at the same temp. Vigorous or explosive polymerisation is caused by $H_2S_2O_8$ at 110°, EtOAc, $EtNO_3$, $CuSO_4$ at 145°, CH_2PhCl, $CH_2{:}CH{\cdot}CH_2Cl$, and Bu$^\gamma$Br. The effect of HNO_3, H_2SO_4, HCl, and AcOH is detailed. The polyethyleneimines studied are obtained by use of HCl or BF_3 under varied conditions. $OH{\cdot}[CH_2]_2{\cdot}NH_2$ is converted by successive treatments with HCl and $SOCl_2$ into *β-chloroethylamine hydrochloride*, m.p. 147·5—148°; β-chloro-*n*-propylamine hydrochloride, m.p. 180—182°, and *N-phenyl-β-chloroethylamine hydrochloride*, m.p. 155—157°, are obtained similarly. $Cl{\cdot}[CH_2]_2{\cdot}NH_2$ polymerises slowly at room temp., rapidly at 40°, suddenly at 95°. Rapid addition of a dil. solution of (**I**) in anhyd. Et_2O to an excess of dry HCl in Et_2O gives the unstable *ethyleneimine hydrochloride*, which rapidly polymerises. *Dimeric* (**I**), b.p. 126—127·5°, is obtained by polymerisation of (**I**) in Et_2O under defined conditions and treatment of the product with NaOH. $NH_2{\cdot}[CH_2]_2{\cdot}NH{\cdot}[CH_2]_2{\cdot}OH$ is converted by distillation under 11 mm. with aq. H_2SO_4 to incipient charring followed by 40% NaOH into piperazine hydrate, m.p. 44°, and (**II**), shown to be identical with dimeric (**I**) by prep. of the *phenylthiocarbamate*, m.p. 129—131°. A polyethyleneimine I, obtained by use of conc. HCl at −78° and then at 25° for many days, is converted (Schotten–Baumann) into the *Bz* derivative, softens (Dennis bar) 110°, which with HCl in $CHCl_3$ yields a *hydrochloride* and is converted into a *CH_2Ph* derivative (*hydrochloride*) by condensation with PhCHO and reduction of the product by Na and abs. EtOH. The *Bz* derivative, softens (Dennis bar) 111°, of a polymeride obtained by use of BF_3 and the *NO*-derivative of a polymeride obtained in H_2O are described. Triethylenetetramine and $C_2H_4Br_2$ in abs. EtOH yield *heptaethyleneoctamine* (**IV**), b.p. 109—110°/0·5 mm. (*Bz* derivative, m.p. 202—220°); *nonaethylenedecamine* (**V**), b.p. 205°/2·5 mm. (*Bz_n* derivative, m.p. 75—105°), is obtained similarly. Attempts to determine the chain length by Van Slyke NH_2-N end-group analysis, cryoscopic measurements on the polymer, and extrapolation of η data obtained with compounds of low mol. wt. are described. For this purpose $(CH_2{\cdot}NH_2)_2$, triethylenetetramine, tetraethylenepentamine, (**IV**), and (**V**) are used. Assuming no branching, the Van Slyke results indicate a degree of polymerisation of 5 units, the cryoscopic method of 42 units, and the extrapolation method of 57 units for a HCl-polymeride. Its non-distillability and relatively high η indicate the unreliability of the NH_2-N method. H. W.

Derivatives of chondrosamine. M. Stacey (*J.C.S.*, 1944, 272—274).—Chondrosamine hydrochloride (**I**) (new prep. from chondroitin sulphate) with Ac_2O in C_5H_5N gives (60% yield) the *α-Ac*$_5$ (**II**), m.p. 178°, $[\alpha]^{20}$ +102° in $CHCl_3$, but with Ac_2O and $ZnCl_2$ yields (30% yield) the *β-Ac*$_5$ derivative (**III**), m.p. 235°, $[\alpha]_D^{20}$ +7° in $CHCl_3$. (**I**) with AgOAc in MeOH–Ac_2O yields α-N-*acetylchondrosamine monohydrate*, m.p. 120—122°, $[\alpha]_D^1$ +115° → 80° after 50 hr. in H_2O. (**II**) with boiling 2% HCl–MeOH gives *N-acetyl-α-methylchondrosaminide*, m.p. 217—218°, $[\alpha]_D^{21}$ +170° in $CHCl_3$, which with MeI–Ag_2O gives the *Me*$_3$ derivative (**IV**), m.p. 185°, sublimes 187°, $[\alpha]_D^{20}$ +121° in $CHCl_3$. With Me_2SO_4 and NaOH, (**II**) gives (**IV**), (**III**) gives *N-acetyltrimethyl-β-methylchondrosaminide* (**V**), m.p. 232°, sublimes 235°, $[\alpha]_D^{20}$ +7° in $CHCl_3$, whilst a mixture of (**II**) and (**III**) gives (**IV**) and (**V**), separated by fractional crystallisation or vac.-sublimation. (**V**) is converted into (**IV**) in boiling HCl–MeOH as for the corresponding glucosamine derivative. (**IV**) on hydrolysis (aq. HCl) yields trimethylchondrosamine hydrochloride, m.p. 178°, $[\alpha]_D$ +114° in H_2O. A mixture of (**II**) and (**III**) with HBr–AcOH affords acetobromochondrosamine (?), m.p. 152°, which loses Br on recrystallising (EtOH), giving *triacetyl-N-acetylchondrosamine monohydrate*, m.p. 183°, $[\alpha]_D^0$ +60° in $CHCl_3$. D. G.

Amino-acids. III. α-Amino-*n*- and -*iso*-butyric acid. J. H. Billmann and E. E. Parker (*J. Amer. Chem. Soc.*, 1944, **66**, 538—539; cf. A., 1944, II, 152).—$NH_2{\cdot}CHEt{\cdot}CH_2{\cdot}OH$, BzCl, and Na_2CO_3 in C_6H_6 at room temp. and then the b.p. give *β-benzamido-*n*-butyl alcohol* (89—91%), m.p. 98—99°, oxidised by $KMnO_4$ in aq. NaOH at 40° [less well, by PbO_2, $Na_2Cr_2O_7$–H_2SO_4, CrO_3, $(NH_4)_2S_2O_8$, or HNO_3] to $NHBz{\cdot}CHEt{\cdot}CO_2H$ (67—72%), m.p. 139—140°, whence boiling 18% HCl yields $NH_2{\cdot}CHEt{\cdot}CO_2H$ (72%). $NH_2{\cdot}CMe_2{\cdot}CH_2{\cdot}OH$ yields similarly the *N-Bz* derivative (78—79%), m.p. 89—90°, and thence $NHBz{\cdot}CMe_2{\cdot}CO_2H$ (91—93%) and $NH_2{\cdot}CMe_2{\cdot}CO_2H$ (86%). R. S. C.

Purity of synthetic *dl*-leucine. D. M. Hegsted and E. D. Wardwell (*J. Biol. Chem.*, 1944, **153**, 167—170).—Leucine (**I**) and *iso*leucine (**II**) are essential for *Lactobacillus arabinosus* (A., 1944, III, 371). When synthetic *dl*-(**I**) is used it is found that (**II**) is no longer necessary, suggesting that natural *l*-(**I**) is free from (**II**) but that synthetic *dl*-(**I**) is not. 7 samples of commercial *dl*-(**I**) were tested by microbiological assay and 5 showed appreciable (**II**) activity. 3 had 10—20% of the activity of (**II**), and from one, (**II**) was isolated. Since *d*-leucine, *tert. dl*-(**I**), and *dl*-norleucine are all without (**II**) activity it is thought that the activity is due entirely to (**II**) or its optical isomerides. J. Ho.

Action of sulphites on cystine disulphide linkages of wool. IV. Methylation of thiol groups of bisulphited wools. S. Blackburn, R. Consden, and H. Phillips (*Biochem. J.*, 1944, **38**, 25—29; cf. A., 1942, II, 426).—SH groups formed when wool is treated with $NaHSO_3$ are methylated by MeBr or MeI. A similar reaction occurs when wool is treated simultaneously with $NaHSO_3$ and Me_2SO_4. *S*-Cysteinesulphonate groups are unaffected by these methylating agents. The isolation of *S*-methylcysteine from hydrolysates of *S*-methylated wools by partition chromatography of the *N*-acetylated NH_2-acids is described. *l-N-Acetyl-S-methylcysteine*, m.p. 73—80°, $[\alpha]_D^{18}$ −37·8° in H_2O, when heated at 100—110° in vac. is converted into dl-N-*acetyl*-S-*methylcysteine*, m.p. 155—156°. J. N. A.

Synthesis of homocystine and of methionine. H. R. Snyder and G. W. Cannon (*J. Amer. Chem. Soc.*, 1944, **66**, 511—512).—2 : 5-Diketo-3 : 6-di-β-chloroethylpiperazine (A., 1943, II, 72) and $CS(NH_2)_2$ in boiling EtOH give the *di-β-isothiuronium chloride* (**I**) (98%), darkens 250°, m.p. 255° (decomp.). Aq. NaOH at room temp. hydrolyses (**I**) to the $(\beta\text{-SH})_2$ compound (not isolated), converted by $FeCl_3$–O_2 into the sulphide (not isolated), which in boiling conc. HCl gives homocystine (74·5%). Gradually adding aq. NaOH to (**I**) and Me_2SO_4 in H_2O at 0° (not other methods) gives the $(\beta\text{-SMe})_2$ compound (75%), m.p. 226—227·5°, and thence *dl*-methionine (65%) (cf. *loc. cit.*). R. S. C.

Allylic rearrangement in the reaction of cuprous cyanide with butenyl halides. J. F. Lane, J. Fentress, and L. T. Sherwood, jun. (*J. Amer. Chem. Soc.*, 1944, **66**, 545—548).—$CHMe{:}CH{\cdot}CH_2X$ or $CH_2{:}CH{\cdot}CHMeX$ (X = Cl or Br) with CuCN at, successively, 60—70°, 95—100°, and 150—160° gives Δ^{β}-*penteno-* (91·5±0·5%) and *α-methyl-*Δ^{β}*-buteno-nitrile* (8·5±0·5%), both b.p. 126° (corr.); the proportions, determined by *n*, are independent of the nature of the org. halide. The reaction is thus by way of the ion, $[CHMe{\cdots}CH{\cdots}CH_2]^+$. R. S. C.

Binary systems formed from nitriles and halides of titanium, tin, and antimony. N. A. Puschin, M. Ristic, I. Parchomenko, and J. Ubovic (*Annalen*, 1942, **553**, 278—285).—HCN and MeCN with $SnCl_4$ give compounds of high m.p. at which they decompose so that the systems cannot be investigated by the method of thermal analysis. Mixtures of HCl and PhCN with $AsCl_3$, of MeCN with $SnBr_4$, PCl_3, $AsCl_3$, AsBr, and $SbBr_3$, and of EtCN or PhCN with $SnBr_4$ remain liquid at room temp. Thermal analysis shows the existence of the following *compounds*, the crystallisation temp. being given in parentheses: $TiCl_4$,EtCN (100°); $TiCl_4$,2PhCN (180°); $TiCl_4$,2$C_6H_4Me{\cdot}CN$-*p*, (153°); $SnCl_4$,2EtCN (76·5°); $SnCl_4$,2PhCN (109°); $SnCl_4$,2-$C_6H_4Me{\cdot}CN$-*o*; (73°); $SnCl_4$,2$C_6H_4Me{\cdot}CN$-*m* (97°); $SnBr_4$,$C_6H_4Me{\cdot}CN$-*o* (53°); $SbCl_3$,$C_6H_4Me{\cdot}CN$-*p* (32°). SbI_3 and PhCN do not afford a mol. compound. H. W.

Ketone series. II. Condensation of monoketones with cyanoacetic acid. D. M. Trachtenberg and M. M. Schemjakin (*J. Gen. Chem. Russ.*, 1943, **13**, 477—480).—$CN{\cdot}CH_2{\cdot}CO_2Et$ reacts with ketones in presence of piperidine for 3 hr. at 110—125°: $CN{\cdot}CH_2{\cdot}CO_2Et + CORR' \rightarrow CRR'{:}CH{\cdot}CN$. The ketones and yields of nitrile in each case are: COMePr, 70%; $COMePr^{\beta}$, 56% of *βγ-dimethyl-*Δ^{α}*-pentenonitrile*, b.p. 70—75°/165 mm.; COMeBu, 61% of *β-methyl-*Δ^{α}*-hexenonitrile*, b.p. 194—196°; $COMe{\cdot}C_6H_{13}$, 65%, b.p. 128—130°/100 mm.; mesityl oxide, 70% of *βδ-dimethyl-*$\Delta^{\alpha\gamma}$*-hexadienonitrile*. F. H.

II.—SUGARS AND GLUCOSIDES.

Interpretation of reactions in the carbohydrate field in terms of consecutive electron displacement. H. S. Isbell (*J. Res. Nat. Bur. Stand.*, 1944, **32**, 45—59).—The general viewpoint is that the peculiar properties of systems involving double linkings may be explained by the migration of electron pairs in the mol. from points of high electron density to points of lower electron density with the addition and elimination of ions. Consideration of apparently unrelated complex reactions of the carbohydrates shows that the formation of the products may be explained by a few simple reactions involving shifts of electron pairs; these include enolisation, de-enolisation,

and double decomp. Mechanisms are presented for the formation of the saccharic acids by the action of alkali on sugars, of unsaturated lactones from OH-acids, of diacetylkojic acid from acetylated glucosone hydrate, for the conversion of glucal triacetate into *ψ*-glucal diacetate, of *ψ*- into *iso*- and proto-glucal, and of tetramethyl-Δ^1-glucosene into *ω*-methoxymethylfurfuraldehyde, for the formation of lævulic acid from *ω*-hydroxymethylfurfuraldehyde and from 2-deoxypentoses and of furfuraldehyde from trimethylpentoses. H. W.

Reaction of glucose with amines. E. Mitts and R. M. Hixon (*J. Amer. Chem. Soc.*, 1944, **66**, 483—486).—Except when R = H, the rate of hydrolysis of glucosylamines, ·CH(OH)·CH(NHR)·O·, parallels the basic dissociation const. of NH_2R; when R = alkyl, equilibrium in ≯2% aq. solution is established in 20 hr. at room temp. after 40% hydrolysis, but when R = aryl, only 8% of hydrolysis has occurred after 90 hr. and when R = acyl, the amides are stable even in acid (at room temp.). The Amadori rearrangement (to ·CO·CH_2·NHR) occurs only when R = aryl, and acid conditions are ideal for prep. of glucosylalkylamines: the Bu, *n*-amyl, *n*-heptyl, and di*cyclo*hexyl derivatives are prepared from glucose (1 mol.) and amine (2 mols.) in 0·5N-HCl at 70—75°; other derivatives are prepared from 1 mol. each of glucose and base in boiling MeOH or EtOH (cf. A., 1944, II, 37). 2-Methylglucose (I) with NHPh·NH_2 and a drop of AcOH in H_2O at room temp. give *2-methylglucosylphenylhydrazine*, m.p. 176—177°, but on further reaction at the b.p. gives glucosephenylosazone; however, with *p*-toluidine in H_2O at 100° (I) gives only *2-methylglucosyl-p-toluidine*, m.p. 150—151°, which does not rearrange or condense further. Hydrogenation (Raney Ni) of the (even non-cryst.) glucosylalkylamines in MeOH, EtOH, or aq. EtOH at, usually, 70—83°/800—1300 lb. gives cryst. alkylglucamines, ·CH(OH)·CH_2·NHR (cf. *loc. cit.*), which are stable to strong acid or alkali and to heat and can be titrated electrometrically with dil. acid; the intermediate alkyl derivatives are surface-active. The following new or revised data (cf. *loc. cit.*) are recorded. Glucosyldi*cyclo*hexylamine, m.p. 97—98°, contains 1 mol. of di*cyclo*hexylamine of crystallisation, which cannot be removed without decomp. *NN'*-Diglucosylethylene diamine, m.p. 152—154° (decomp.). Glucosyl-*n*-hexa-, m.p. 106—107° after softening, and -*n*-octa-decylamine, m.p. 104—105° after softening. *N*-*n*-Butyl-, m.p. 127—128°, *N*-*n*-amyl-, $[\alpha]_D^{25}$ −13·8° in 50% EtOH. *N*-*n*-hexadecyl-, m.p. 123—124° after softening, *N*-*n*-octadecyl-, m.p. 118—119° after softening, N-iso*propyl*-, m.p. 126—127° after softening, $[\alpha]_D^{25}$ −13° in 50% EtOH, and *N*-*β*-*octylglucamine*, m.p. 107—108° after softening. NN'-*Propylenedigluc-amine*, m.p. 135—137°. 1-Aminoglucose, m.p. 120—121°, $[\alpha]_D^{24}$ +19·1° in H_2O, is stable in H_2O at room temp. and can be titrated potentiometrically with dil. acid. R. S. C.

Large-scale preparation of *D*-altrose. *D*-Altroseoxime and its rate of mutarotation. R. C. Hockett and L. B. Chandler (*J. Amer. Chem. Soc.*, 1944, **66**, 627—628).—Prep. of cryst. *D*-altrose (*oxime*, m.p. 143—144°, $[\alpha]_D^{24\cdot2}$ −64·0° → −9·8° in H_2O, from *D*-lactose (cf. Richtmyer *et al.*, A., 1935, 1355) is modified to give 3·7% over-all yield. R. S. C.

Preparation of mannose. E. K. Narayanan (*Indian J. Med. Res.*, 1941, **29**, 1—6).—Complete hydrolysis to mannose of the polysaccharide in ivory-nut meal requires 10 hr. boiling with N-H_2SO_4 or 15 hr. heating at 105°. About 7% of the total sugar is thereby destroyed. S. E. M.

Magnitude of " unit chains " of liver-glycogen of rabbits supplied with glucose, fructose, and sucrose.—See A., 1944, III, 606.

Glycosides sensitive to alkali. Glucosides of nitro-alcohols. B. Helferich and M. Hase (*Annalen*, 1943, **554**, 261—268).—Presence of NO_2, like that of SO_3H, in immediate propinquity to the glycosidic linking renders the glycosides very sensitive to alkali and hence enables them to reduce Fehling's solution immediately. Even under mild conditions the glucose liberated by alkaline hydrolysis immediately darkens. NO_2 remote from the glycosidic linking does not cause sensitiveness to alkali. The action of Ag_2CO_3 on a solution of acetobromoglucose (I) and NO_2·$[CH_2]_2$·OH in $CHCl_3$ at room temp. leads to *β-nitroethyl-β-d-glucoside tetra-acetate*, m.p. 119—120° (corr.), $[\alpha]_D^{\ 5}$ −15·8° in $CHCl_3$, which could not be hydrolysed to the free glucoside; replacement of Ag_2CO_3 by Ag_2O and $CaSO_4$ gives (?) *β-nitroethyl-α-d-glucoside tetra-acetate*, m.p. 139—140° (corr.), softens at ~125°, $[\alpha]_D^{\ 5}$ +37·5° in $CHCl_3$. NO_2·$CH(CH_2$·OH$)_2$, (I), and Ag_2CO_3 in anhyd. Et_2O yield *β-nitropropane-αγ-dioldi-β-d-glucoside tetra-acetate*, m.p. 179·5—180·5° (corr.), $[\alpha]_D^{20\cdot5}$ −25·8° in $CHCl_3$. NO_2·$C(CH_2$·OH$)_3$, (I), and Ag_2CO_3 in EtOAc afford *β-nitro*-iso*butanetriol-β-d-glucoside* (*nitro*iso*butylglycerol-β-d-glucoside*) *tetra-acetate*, m.p. (anhyd.) 132—134° (corr.), (+1H_2O), m.p. 94·5—96°, $[\alpha]_D^{\ 1}$ −31·2° in MeOH; under similar conditions but with substitution of $COMe_2$ for EtOAc the *product* appears to be NO_2·$C(CH_2$·OH$)_2$·CH_2·O·CMe_2·O·$C_6H_7O(OAc)_4$, m.p. (very indef.) 154—156°/corr.), $[\alpha]_D^{19}$ −8·8° in $CHCl_3$; the substances are converted by Ac_2O and C_5H_5N at 0° and subsequently at room temp. into the corresponding *hexa-acetates*, m.p. 147—148° (corr.), $[\alpha]_D^{21}$ −24·1° in $CHCl_3$, and m.p. 144—146°, $[\alpha]_D^{20\cdot5}$ −18·1° in $CHCl_3$. *δ-Nitro-n-butanol-β-d-glucoside tetra-acetate* (II), m.p. 139—141° (corr.), $[\alpha]_D^{21}$ −18·7° in $CHCl_3$, is obtained from the corresponding I-compound and $AgNO_2$ in boiling C_6H_6; it reduces Fehling's solution only after hydrolysis and is converted by NaOH into the amorphous glucoside, re-acetylated to (II). H. W.

Cerebroglucoside, m.p. 185°, $[\alpha]_D^{14}$ −11·3° in C_5H_5N, from spleen, its H_2-derivative, m.p. ~188°, $[\alpha]_D^{27}$ −2·6°, and lignoceryldihydrosphingosine.—See A., 1944, III, 549.

Chemistry and biochemistry of plant materials. IX. Formation of dihydroflavonol and flavonol and synthesis of chalconeflavanone-flavonol glucosides. L. Reichel and J. Steudel (*Annalen*, 1942, **553**, 83—97).—Resacetophenone-4-glucoside (I) is used in further syntheses. Resacetophenone, *α*-acetobromoglucose, and 10% NaOH in $COMe_2$ at room temp. afford resacetophenone-4-glucoside tetra-acetate (cf. Müller, *Diss., Karlsruhe*, 1938), m.p. 130—131°, $[\alpha]_D^{20}$ −29·7° in $COMe_2$, hydrolysed by gradual addition of Na to its solution in abs. MeOH to (I), m.p. 198—200°, $[\alpha]_D^{20}$ −86·9° in $COMe_2$. PhCHO, (I), and 2N-NaOH give *2′ : 4′-dihydroxychalkone-4′-β-d-glucoside* (II), m.p. 195—197°, (+1H_2O), $[\alpha]_D^{20}$ −53·9° in $COMe_2$, hydrolysed by acid to 2′ : 4′-dihydroxychalkone, m.p. 147—148°. (II) is oxidised by alkaline H_2O_2 to *3 : 7-dihydroxyflavone-7-β-d-glucoside*, m.p. 223—225°, $[\alpha]_D^{20}$ −90·1° in dioxan, slowly hydrolysed by acid to 7-hydroxyflavonol, m.p. 252—254°. (II) is converted by dil. NaOH–aq. EtOH into *7-hydroxyflavanone-7-β-d-glucoside*, m.p. 184—187°, (+1H_2O), $[\alpha]_D^{20}$ −102·6° in $COMe_2$, also obtained slowly from (I), PhCHO, and NaOH in aq. EtOH at room temp. and hydrolysed by acid to 7-hydroxyflavanone, m.p. 182—184°. *iso*-Vanillin, (I), and NaOH at room temp. yield *3 : 2′ : 4′-trihydroxy-4-methoxychalkone-4′-β-d-glucoside* (*4-methylbutein-4′-glucoside*), m.p. 212—214°, (+1·5H_2O), $[\alpha]_D^{20}$ −45·2° in $COMe_2$, oxidised by alkaline H_2O_2 to *3 : 7 : 3′-trihydroxy-4′-methoxyflavone-7-β-d-glucoside*, m.p. 254—255° (decomp.), $[\alpha]_D^{20}$ −59·3° in C_5H_5N, and converted by a little NaOH in aq. MeOH into *7 : 3′-dihydroxy-4′-methoxyflavanone-7-β-d-glucoside*, m.p. 208—211°, (+1H_2O), $[\alpha]_D^{20}$ −84·3° in 50% $COMe_2$. H. W.

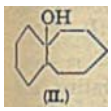
Chemistry and biochemistry of plant materials. X. Synthesis of flavanoneglucosides under physiological conditions. L. Reichel and R. Schickle (*Annalen*, 1942, **553**, 98—102).—Negative results are obtained by the attempted condensation of hydroxyacetophenones with hydroxybenzaldehydes to hydroxychalkones or hydroxyflavanones under physiological conditions so that the biosyntheses of these compounds does not occur in this manner. Since these compounds are found in plants almost exclusively as glucosides it is highly improbable that the latter are formed in the cell from aglycone and sugar under the influence of carbohydrases. The authors have therefore examined the possibility that glycosides of the OH-compounds condense with one another and that the sugar residues are partly or wholly removed from the products by sp. enzymes; glycosides may then be resynthesised from these secondary aglycones. Resacetophenone-4-*β*-*d*-glucoside (I) and PhCHO at pH 8·3 give a 20% yield of 7-hydroxyflavanone-7-*β*-*d*-glucoside, m.p. 184—187°, in 83 days; small additions of carotene are used as an antioxidant of PhCHO. 4′-Hydroxyflavanone-4′-*β*-*d*-glucoside, m.p. 218—220°, $[\alpha]_D^{12}$ −37·4° in dioxan, is obtained in 19% yield at pH 8·0 in 103 days from *o*-OH·C_6H_4·COMe and *p*-hydroxybenzaldehyde-*β*-*d*-glucoside, m.p. 156—158° (obtained by hydrolysis of the tetra-acetate, m.p. 144—145°, prep. from *p*-OH·C_6H_5·CHO and *α*-acetobromoglucose by NaOH in $COMe_2$). *o*-OH·C_6H_4·COMe and *2 : 4-dihydroxybenzaldehyde-4-β-d-glucoside*, m.p. 218—220°, $[\alpha]_D^{12}$ −102·1° in H_2O, afford 2′ : 4′-dihydroxyflavanone-4′-*β*-*d*-glucoside, m.p. 180—183° (decomp.), (+ 2H_2O), $[\alpha]_D^{12}$ −47·1° in abs. MeOH; at pH 7·6 the yield is 23% after 40 days and at pH 8·3 it is only 12% after 63 days. (I) and *iso*vanillin-*β*-*d*-glucoside afford *7 : 3′-dihydroxy-4′-methoxyflavanone-7 : 3′-β-d-diglucoside*, m.p. 220—224°, $[\alpha]_D^{18}$ −124·3° in quinoline (also + 2H_2O); the yield is 20·4% in 83 days at pH 7·5 and 14·6% in 80 days at pH 8·4. H. W.

III.—HOMOCYCLIC.

Isomerisation of polymethylene hydrocarbons under the influence of aluminium chloride. X. Isomerisation of methyl*cyclo*heptane. M. B. Turova-Polak and P. L. Rappoport (*J. Gen. Chem. Russ.*, 1943, **13**, 353—357).—Over Pt-C at 305—310°, methyl*cyclo*heptane (I) is isomerised and dehydrogenated directly, in 94% yield, to xylene (*p*-, with a small proportion of *m*-). Bromination of (I) in the presence of $AlBr_3$ yields tetrabromoxylene, m.p. 253°. Addition of $AlCl_3$ to (I) causes a rapid rise of temp. and conversion of (I) into 1 : 4-dimethyl*cyclo*hexane, containing a very small amount of the 1 : 3- and a trace of the 1 : 2-compound. R. C. P.

Carbon rings. XXXV. Preparation of *cyclo*undecane from benzosuberane. P. A. Plattner (*Helv. Chim. Acta*, 1944, **27**, 801—810).—Gradual addition of Ph·$[CH_2]_4$·COCl in much CS_2 to $AlCl_3$ in boiling CS_2 affords benzosuberone, b.p. 138—139°/12 mm., in 87% yield. This is reduced (Clemmensen–Martin) to benzosuberane (I), b.p. 99·8—100°/13 mm., m.p. −1·5°, which is hydrogenated (PtO_2 in AcOH or Raney Ni–H_2 at 180°/145 atm.–EtOH) to *hexahydro-*

benzosuberane (*dicyclo*-[0 : 4 : 5]-*undecane*), b.p. 88·5—89°/11 mm. Ozonisation then yields mainly *dicyclo*-[0 : 4 : 5]-*undecan*-1-*ol* (II), b.p. 118—120°/13 mm., m.p. 30—31° (*dinitrobenzoate*, m.p. 201°), with minor amounts of cyclo*undecane*-1 : 6-*dione* (III), b.p. 110—115°/0·1 mm. [*dioxime* (IV), m.p. 232—234° (decomp.); *disemicarbazone*, m.p. 218°]; a *semicarbazone*, m.p. 154°, of a dicyclic monoketone is also isolated. Addition of MnO_2 favours the formation of (II) but unchanged material in considerable proportion remains. (II) is converted by anhyd. $ZnCl_2$ at 140° into *dicyclo*-[0 : 4 : 5]-*undecene* (III), b.p. 90—91°/12 mm., which when ozonised in 50% AcOH at −10° affords (III). More conveniently (III) is obtained by hydrogenation of (I) by Ca hexammine. Reduction of (IV) by Na and C_6H_{11}·OH leads to a mixture of amines from which 1 : 6-*diamino*cyclo*undecane*, b.p. 156—158°/12 mm., is readily isolated through the sparingly sol. carbamate. It gives a *dihydrochloride*, decomp. 230—260° with partial sublimation, *dipicrate*, m.p. 233—235°, and an Ac_2 derivative, m.p. 252·3—252·5°. It is methylated to 1 : 6-*tetramethyldiamino*cyclo*undecane dimethiodide*, decomp.312—313°; the corresponding quaternary base is decomposed thermally into *cyclo*undecadiene, which is readily hydrogenated (PtO_2 in EtOH–Et_2O at room temp.) to cyclo*undecane*, b.p. 91—91·3°/12 mm., m.p. −7·3°. H. W.



(III.)

Binary system, tin tetrachloride–*m*-dinitrobenzene. E. Hertel (*Annalen*, 1942, **553**, 286—288; cf. A., 1933, 27).—In reply to Puschin *et al.* (A., 1943, II, 4) it is stated that in the examination of the system $TiCl_4$–*m*-$C_6H_4(NO_2)_2$ the authors have so worked that in the region up to 50 mol.-% of $TiCl_4$ the compound $2TiCl_4.C_6H_4(NO_2)_2$ is invariably formed in the primary crystallisation from the undercooled melt either spontaneously or by seeding. The eutectic between the phases $2TiCl_4.C_6H_4(NO_2)_2$ and *m*-$C_6H_4(NO_2)_2$ happens to be at ~50 mol.-% of $TiCl_4$. Lack of suitable seeding material has prevented the discovery of other phases. H. W.

Valency tantomerism or mesomerism with ωω′-tetraphenylpolyenes. G. Wittig and B. Fartmann (*Annalen*, 1943, **554**, 213—240).—Chemical and physical methods of discriminating between valency tautomerism and mesomerism are discussed at the instances of *p*-vinylenedi(triphenylmethyl) (I), *p*- (II) and *m*- (III) -azoditriphenylmethyl. (*p*-$C_6H_4Bz{\cdot}CH_2)_2$ is converted by Br in boiling $PhNO_2$ into *pp′*-dibenzoylstilbene, m.p. 234—235°, transformed by the successive action of LiPh in anhyd. Et_2O and H_2O into *pp′*-di(hydroxydiphenylmethyl)stilbene, m.p. 218—218·5°, which with HCl gives *pp′*-di(chlorodiphenylmethyl)stilbene, decomp. 213—216° when heated from 100° or decomp. 234° (bath preheated to nearly 234°). This with MeOH in hot dioxan gives pp′-*di*(*methoxydiphenylmethyl*)*stilbene*, m.p. 178—179°, and is dehalogenated by Cu powder (apparatus see C., 1944, Part 4) to (I), m.p. 252—255°. Its solutions are immediately decolorised by O_2 without manifestation of the Schmidlin phenomenon. *p*-$NO_2{\cdot}C_6H_4{\cdot}CPh_2Cl$, m.p. 92—93°, is converted by NaOAc and AcOH into the corresponding carbinol (IV), reduced by Zn dust and NaOH in aq. EtOH to *pp′*-di(hydroxydiphenylmethyl)hydrazobenzene (V) which, on account of its instability, is immediately oxidised to pp′-*di*(*hydroxydiphenylmethyl*)*azobenzene* (VI), m.p. 218—219°, either by Br and NaOH or, preferably, by CrO_3 in aq. AcOH. Electrolytic reduction of (IV) at a Pt cathode gives pp′-*di*(*hydroxydiphenylmethyl*)*azoxybenene*, m.p. 177—179°, and then (very slowly) (VI). (VI) is transformed by HCl in C_6H_6 containing a little AcCl into pp′-*di*(*chlorodiphenylmethyl*)*azobenzene*, decomp. 242° [corresponding $(OMe)_2$-derivative, m.p. 200—201°, softens at 198°], converted by Cu powder in C_6H_6, PhMe, or CCl_4 into (II), almost black crystals, m.p. 252—255°, which markedly depresses the m.p. of (I). Solutions of (II) are immediately and non-recurringly decolorised by air with the formation of complex peroxides ·O·O·$CR_2{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_4{\cdot}CR_2{\cdot}O{\cdot}O{\cdot}CR_2$···. Formation by use of Cu powder and behaviour towards air indicate a diradical structure for (II); the possible quinonoid structure, suggested by its formation by dehydration of (V), is negatived by its prolonged stability towards dil. H_2SO_4 at 60°, which also brings evidence against a tautomerism of two valency isomerides in solution. Since the magnetic properties of the analogous (I) exclude the possibility that these polyenes exist solely in the diyl form it appears highly probable that internal valency compensation has occurred between the conjugated systems of a quinone and a diradical and therefore that the polyene mol. is in a condition intermediate between the limiting structures of a quinone and a diyl. COPh·$C_6H_4{\cdot}NO_2$-*m* is transformed by PCl_5 at 120—130° into m-*nitrobenzophenone dichloride*, m.p. 66°, converted by $AlCl_3$ and C_6H_6 into m-*nitrotriphenylmethyl chloride*, m.p. 92—93°, which with NaOAc yields the carbinol, m.p. 75°. This is reduced electrolytically (Pb anode; Ni cathode) to mm′-*di*(*hydroxydiphenylmethyl*)*azobenzene*, m.p. 174—176°, which is converted by HCl and AcCl in $CHCl_3$ into mm′-*di*(*chlorodiphenylmethyl*)*azobenzene*, m.p. 206—208° [corresponding $(OMe)_2$-derivative, m.p. 200—201°], transformed by Cu powder in absence of air and light into (III), which could not be obtained cryst. Its solutions are pale brown with a tendency towards green resembling in shade and depth those of CPh_3. (III) behaves as a true diradical dissociated to only a slight extent; at 80° the colour becomes considerably more intense but the original shade is regained on cooling. The structure of (I), (II), and (III) is confirmed by their conversion into the corresponding dichlorides by $PhICl_2$. With Li-diphenylamine in Et_2O the dichlorides yield the corresponding diyls. From solutions of (I) and (II) mixed crystals of the compounds are obtained. (I) and (III) do not yield cryst. materials and definite products could not be isolated from (II) and (III).

The dependence of absorption spectrum on temp. opens a new way for discriminating between mesomerism and valency tautomerism. In 0·0001M. solution the varying colour of the solutions with temp. is obvious; association is excluded since the solutions obey Beer's law. The violet-blue colour of (I) passes into blue at −70° and becomes non-characteristic at 100°. (II) is more violet than (I); on cooling the colour is displaced towards shorter λ, on heating towards longer λ; at 100° it appears almost carmine-red. Difficulties due to apparatus prevent quant. measurements within such wide limits but between 15° and 55° the absorption max. [~590 mμ. for (I) and ~575 mμ. for (II)] is displaced towards shorter λ with increase of temp. Optical measurements could not be made with (III) since its max. lies at the short-wave border of the visible spectral region. H. W.

Hydrogenation of anthracene by tetrahydronaphthalene. M. Orchin (*J. Amer. Chem. Soc.*, 1944, **66**, 535—538).—In presence of Pd–C in an open tube, 1 : 2 : 3 : 4-tetrahydronaphthalene (I) at 225—230° evolves much H_2. Presence also of anthracene (II) decreases evolution of H_2, which is utilised for hydrogenation of the (II) to mainly 1 : 2 : 3 : 4-tetra- (III) with some 9 : 10-di- (IV) and *s*-octahydroanthracene. The amounts of H_2 and hydrogenated products depend on the temp. and ratio of (I) to (II). Reaction in a sealed tube is similar. The di- and octa-hydroanthracene are formed by disproportionation of the H_4-compound, a reaction which is shown to be reversible. With Raney Ni in boiling EtOH, (II) or (IV) gives a good yield of (III). In presence of Pd–C *cyclo*hexenone acts as a dihydrophenol and with (II) gives 30% of (III). These reactions show the need for caution in determining the primary products of hydrogenation of, *e.g.*, coal. Chromatographic separation of (III) and (IV) on Al_2O_3 is described. R. S. C.

Hydroanthracenes and hydrophenanthrenes. II. J. W. Cook, (Miss) N. A. McGinnis, and S. Mitchell (*J.C.S.*, 1944, 286—293; cf. A., 1939, II, 103).—*trans*-Hexahydroanthrone [$(NO_2)_1$-, m.p. 130·5—131·5°, and $(NH_2)_1$-derivative, m.p. 165—166°] is reduced (Zn–HCl) to trans-as-*octahydroanthracene* (I), m.p. 63—64°, and a little (?) *hexadecahydro*-9 : 9′-*dianthryl*, m.p. 245—250°, but with H_2–PtO_2 yields (I) and 9-*hydroxy*-trans-as-*octahydroanthracene*, m.p. 136°, giving a *hexahydroanthracene*, m.p. 63—66°, on dehydration. Sulphonation of (I) gives the *Na sulphonate*, converted by fusion with KOH into ar-*hydroxy*-trans-as-*octahydroanthracene*, m.p. 104°, affording *trans-cyclo*hexane-1 : 2-diacetic acid, m.p. 166—167°, on oxidation ($KMnO_4$). With $AlCl_3$ (I) yields a *perhydroanthracene* (II), m.p. 204°, and on catalytic hydrogenation (PtO_2) gives a *perhydroanthracene* (III), m.p. 39—40°, or (Raney Ni) at 200°/150 atm. a perhydroanthracene (IV), m.p. 89—90°. Hydrogenation of *s*-octahydroanthracene yields (Raney Ni) a mixture of (III) and (IV) and (PtO_2) a perhydroanthracene (V) (completely *cis*?), m.p. 61·5—63°. With $AlCl_3$ (V) is converted into (III) and (III) into (IV). (II) and (IV) are not dehydrogenated by Se or Pd but (V) with Se affords anthracene. $AlCl_3$ with crude *as*-octahydrophenanthrene (VI) (from cyclisation of 1-β-phenylethyl-Δ¹-*cyclo*hexene with $AlCl_3$) at 50—70° effects *cis–trans*-isomerisation, oxidation (CrO_3) of the product giving *trans*-9-keto-*as*-octahydrophenanthrene, m.p. 95—96° (oxime, m.p. 176—177°), but at 125—130° tetrahydronaphthalene, (II), and (IV) are obtained. Structures are suggested for (II), (III), and (IV). 2-β-Phenylethyl*cyclo*hexylacetyl chloride (corresponding p-*phenylphenacyl* ester, m.p. 75—77°) with $AlCl_3$ in $PhNO_2$ gives a *dibenzocyclooctanone* (2 : 4-*dinitrophenylhydrazone*, m.p. 242—244°), and with $SnCl_4$ in C_6H_6 a *lactone*, $C_{16}H_{20}O_2$, m.p. 67—68°. 2-Benzyl*cyclo*pentylacetyl chloride with $AlCl_3$ yields 1 : 2 : 3 : 4 : 7 : 8 : 9 : 10-*octahydro*-5 : 6-*benz*-7-*azulone*, m.p. 56° (2 : 4-*dinitrophenylhydrazone*, m.p. 169—170°), giving the *octahydrobenzazulol*, m.p. 128—129°, dehydration of which gives 1 : 2 : 3 : 4 : 9 : 10-hexahydrobenzazulene, m.p. 29—35°, affording 1 : 2 : 3 : 4 : 7 : 8 : 9 : 10-*octahydrobenzazulene*, m.p. 29—30°, on hydrogenation. M.p. are corr. D. G.

Influence of *n*-alkyl groups on the rate of a cyclisation reaction. E. Berliner (*J. Amer. Chem. Soc.*, 1944, **66**, 533—535).—Cyclisation of *o*-CHPhMe·$C_6H_4{\cdot}COR$ to dialkylanthracenes in boiling 48% HBr–AcOH depends on the nature of R (cf. Bradsher *et al.*, A., 1943, II, 95), *k* being R = Me 4·6, Et 1·8, Pr^{α} 0·99, Bu^{α} 0·35, *n*-amyl 0·36, *n*-C_6H_{13} 0·36, Ph 0·16, and CH_2Ph 0·91 × 10^{-2} min.$^{-1}$ With less conc. acid the rate for R = Me is greatly reduced. Ring-closure probably occurs by way of *o*-CHMePh·$C_6H_4{\cdot}C^+R{\cdot}OH$, the rate being governed by the inductive effect of R. Adding *o*-$C_6H_4Cl{\cdot}COCl$ in C_6H_6 to $AlCl_3$–C_6H_6, keeping at room temp., and then boiling gives *o*-$C_6H_3Cl{\cdot}COPh$ (85·7%), m.p. 43—44°, b.p. 178—180°/14—15 mm. (lit. an oil), whence MgMeCl yields *o*-$C_6H_4Cl{\cdot}CPh{:}CH_2$ (77%), b.p. 164—166°/17 mm. H_2–Raney Ni in EtOH at 1 atm. then yields α-*phenyl*-α-*o*-*chlorophenylethane*, b.p. 158°/12 mm., which with CuCN and C_5H_5N (bath at 250—260°) gives *o*-$CN{\cdot}C_6H_4{\cdot}CHPhMe$

(75·7%), b.p. 190—191°/17—18 mm. With, successively, MgRCl–C_6H_6, 20% aq. NH_4Cl, and boiling HCl–$COMe_2$–H_2O this gives o-α-*phenylethyl-aceto-* (75·5%), b.p. 184—186°/16—17 mm., *-propio-*, b.p. 189—190°/16—17 mm., -n-*butyro-*, b.p. 194—197°/14—15 mm., -n-*valero-*, b.p. 205—206°/17—18 mm., -n-*hexo-*, b.p. 209—212°/15—16 mm., -n-*hepto-*, b.p. 217—219°/14—15 mm., and *-ω-phenyl-aceto-phenone*, b.p. 195—197°/1—2 mm., and 2-α-*phenylethylbenzophenone*, m.p. 47—48°, b.p. 216—219°/7—8 mm. Cyclisation (cf. above) yields 9-*methyl*-10-*ethyl-*, m.p. 143·2—144° (*picrate*, m.p. 137·8—138·4°), -10-n-*propyl-*, m.p. 97·8—98·6° (*picrate*, m.p. 125·5—126·2°), -10-n-*butyl-*, m.p. 78·2—78·8° (*picrate*, m.p. 91·8—92·8°), -10-n-*amyl-*, m.p. 71—71·8° (*picrate*, m.p. 85·4—86·2°), and -10-n-*hexyl-*, m.p. 65·8—66·5° (*semipicrate*, m.p. 78·2—79·2°), 9-phenyl-10-methyl-, m.p. 113·5—114·5° (lit. 112°) (*picrate*, m.p. 125·2—126°), and 9-*benzyl*-10-*methyl-*, m.p. 167·8—168·6°, *-anthracene*. M.p. are corr. R. S. C.

Hydrogenolysis of abietic acid. H. B. Charmbury and C. C. Wright (*J. Amer. Chem. Soc.*, 1944, **66**, 526—532).—Hydrogenolysis of abietic acid for 2 hr. at 325°, 370°, 400°, 425°, and 450°, and for 3 discontinuous periods each of 1 hr. at 400°, is investigated. Decarboxylation to yield CO_2 accounts for almost all the loss of O_2; in 2 hr. it is incomplete at 325° but complete at 450°, and at 400° 73·9% complete in 1 hr.; some CO + H_2O are also obtained, being derived at least partly by reduction of CO_2. Loss of Pr^{β} does not occur at 375° but is rapid at higher temp., being then a function of $[H_2]$ or partial pressure of H_2. The amounts of CH_4, C_3H_8, *n-* and *iso*-C_4H_{10} formed show that the C_2H_6 results partly from cracking of C_3H_8, but that loss of 1 Me begins at 325° and is also a function of time and $[H_2]$. At 370° there is some addition of H_2 to C:C or C:C·C:C, but at higher temp. dehydrogenation occurs. Ring-fission begins at 425°, thereafter becoming more rapid and being a function of $[H_2]$; products isolated include *trans*-1: 2-dimethyl-, methyl-, and ethyl-*cyclo*hexane, 3 : 5-dimethyl-Δ^1-*cyclo*hexene, and, by isomerisation of a C_6-ring, 1 : 3-dimethyl*cyclo*pentane. The H_2 consumed at lower temp. is almost all accounted for by saturation of C:C, cracking, and reduction of CO_2. The following products are isolated: at 370° 12-*methyl*-$\Delta^{9(14)}$-*dodecahydroretene*, b.p. 139—142°/4 mm.; at 400° (2 hr.) 1 : 12-*dimethyl*-$\Delta^{7:9(14)}$-*decahydrophenanthrene*, b.p. 122—125°/4 mm., and 12-*methyldecahydroretene*, b.p. 143—146°/5·5 mm., and by discontinuous heating two isomeric decahydroretenes, b.p. 122—128°/4 mm., and 1 : 12-*dimethyl-*, b.p. 127—130°/3 mm.; and then 1-*methyl-dodecahydrophenanthrene*, b.p. 127—131°/2 mm.; at 425° 1-*methyl*-$\Delta^{7\cdot9(14)}$-*decahydro-*, b.p. 118—120°/3 mm., and at 450° 1-*methyloctahydro-phenanthrene*, b.p. 112—116°/4 mm. R. S. C.

Aryl and aralkyl carbamides. J. S. Buck, R. Baltzly, and A. E. Ardis (*J. Amer. Chem. Soc.*, 1944, **66**, 311—312).—NH_2·CO·NH·NO_2 and NHRR′ (reaction incomplete for *o*-substituted amines) give N-*phenyl*-N-β-*hydroxyethyl-*, m.p. 110°, and N-m-4-*xylyl-*, m.p. 73—74°, N-5-*chloro*-o-*tolyl-*, m.p. 93°, N-5-*bromo*-o-*tolyl-*, m.p. 88·5—89°, N-4-*chloro*-o-*tolyl-*, m.p. 166—167°, N-3-*bromo*-p-*tolyl-*, m.p. 116°, N-4-*bromo*-2-*ethylphenyl-*, m.p. 95°, N-p-*ethylphenyl-*, m.p. 122—124°, N-2-*bromo*-4-*ethylphenyl-*, m.p. 114°, and N-5-*bromo*-o-*phenetyl*-N-*ethylcarbamide*, m.p. 124—124·5°, N-*benzyl-*, m.p. 135°, N-p-*methoxybenzyl-*, m.p. 140—141°, N-3-*chloro*-4-*methoxybenzyl-*, m.p. 169—169·5°, N-3-*bromo*-4-*methoxybenzyl-*, m.p. 178°, N-β-3-*chloro*-4-*methoxyphenylethyl-*, m.p. 117·5—118°, and N-β-3-*bromo*-4-*methoxyphenylethyl*-N-*methylcarbamide*, m.p. 116·5—117°, N-5-*bromo*-o-*tolyl*-N-n-*propyl-*, m.p. 94·5—95·5°, N-4-*chloro*-o-*tolyl*-N-n-*butyl-*, m.p. 79·5—80°, and N-*benzyl*-N-n-*butyl-carbamide*, m.p. 61—62°. EtNCO and the appropriate amine give N-5-*bromo*-o-*tolyl*-N′-*ethyl-*, m.p. 230—232°, and N-m-4-*xylyl*-NN′-*diethyl-carbamide*, m.p. 76°. *o*-C_6H_4Et·NEt·CO·NH_2 with BzCl–NaOH or –C_5H_5N gives NN-*dibenzoyl*-N′-*o-ethylphenyl*-N′-*ethylcarbamide*, m.p. 128—129°. The following amines are prepared by standard methods: NHRMe in which R = 4 : 3 : 1-OMe·C_6H_3Cl·CH_2 (*hydrochloride*, m.p. 201—201·5°), -OMe·C_6H_3Br·CH_2 (*hydrochloride*, m.p. 202—203°), -OMe·C_6H_3Cl·$[CH_2]_2$ (*hydrochloride*, m.p. 196°), and -OMe·C_6H_3Br·$[CH_2]_2$ (*hydrochloride*, m.p. 215—216°); NHREt in which R = 2 : 4 : 1-C_6H_3MeCl, b.p. 136°/13 mm., -C_6H_3MeBr, b.p. 96—99°/0·25 mm., and -C_6H_3EtBr, b.p. 135°/3 mm., 4 : 2 : 1-C_6H_3MeBr, b.p. 137°/17 mm., and -C_6H_3EtBr, b.p. 107°/3 mm., 2 : 5 : 1-C_6H_3MeCl, b.p. 141°/27 mm., and -OEt·C_6H_3Br, b.p. 111°/0·25 mm., and *p*-C_6H_4Et, b.p. 122—123°/22 mm.; 2 : 5 : 1-C_6H_3MeCl·$NHBu^{\alpha}$, b.p. 125°/1 mm. M.p. are corr. R. S. C.

Metabolism of 2 : 4 : 6-trinitrotoluene (α-T.N.T.). H. J. Channon, G. T. Mills, and R. T. Williams (*Biochem. J.*, 1944, **38**, 70—85).—2 : 6 : 2′ : 6′-Tetranitro-4 : 4′-azoxytoluene, m.p. 215—216°, is obtained by oxidation of 2 : 6 : 1 : 4-$(NO_2)_2C_6H_2Me$·NH·OH with $K_2Cr_2O_7$ and H_2SO_4 or, preferably, of 2 : 6 : 1 : 4-$(NO_2)_2C_6H_2Me$·NH_2 (I) with $(NH_4)_2S_2O_8$. Treatment of α-T.N.T. with H_2S–NH_3–EtOH gives (I), converted into its *Bz*, m.p. 263—264°, and *PhSO*$_2$ (II), m.p. 175—177°, derivatives. Electrolytic reduction of α-T.N.T. affords a mixture of dinitroaminotoluenes (III) from which after benzoylation 2 : 4-*dinitro*-6-*benzamidotoluene*, m.p. 216—217°, is isolated. (III) is more conveniently separated into its components by treatment with $PhSO_2Cl$ and C_5H_5N, which leads to the isolation of 2 : 4-*dinitro*-6-*dibenzenesulphonamidotoluene*, m.p. 222°, and (II) (m.p. 177—178°). These are hydrolysed to 2 : 4-*dinitro*-6-*aminotoluene*, m.p. 176° (*Ac* derivative, m.p. 159—160°), and (I), respectively. (See also A., 1944, III, 606, and C., 1944, 118.) H. W.

***p*-Hydroxylaminobenzenesulphonamide, its acetyl derivatives and diazotisation reaction.** H. Bauer and S. M. Rosenthal (*J. Amer. Chem. Soc.*, 1944, **66**, 611—614).—*p*-NO_2·C_6H_4·SO_2·NH_2 and Zn dust in NH_4Cl–EtOH–H_2O at 45—52° give *p*-OH·NH·C_6H_4·SO_2·NH_2 (I) (63—88·5%), m.p. 143—144° (decomp. 148—158°) (lit. 139·5—140·5°), the mother-liquors from which with $FeCl_3$ yield p-*nitrosobenzenesulphonamide*, decomp. 155—268°. With $NaNO_2$–aq. HCl, (I) gives the N^4-*NO-*, m.p. 120°, with Ac_2O gives the N-*Ac*, m.p. 228° (cannot be diazotised), but with Ac_2O in much H_2O gives mainly the O-*Ac* derivative (II), m.p. 138° (readily diazotised). *p*-NO_2·C_6H_4·CO_2H and Zn dust in NH_4Cl–NaOH–H_2O at 15—20° give p-*hydroxylaminobenzoic acid* (III) (31%), darkens ~240°, m.p. >300° [N-*Ac*, m.p. 210° (decomp.), and *N*-NO-derivative, decomp. when heated]. In AcOH the products obtained from (I), (II), (III), and NHPh·OH by HNO_2 contain 23, 63—67, 45%, and a trace, respectively (determined colorimetrically), of diazo-compound. Addition of Ac_2O prior to treatment of (I), (III), and NHPh·OH increases these amounts to 48, 63, and 10%, respectively. Use of this reaction to determine (I) in body fluids is liable to error owing to interference by other labile compounds. R. S. C.

N^4-Benzoyl-N^1-acetylsulphanilamide. C. P. Lo and L. J. Y. Chu (*J. Amer. Chem. Soc.*, 1944, **66**, 660).—N^4-*Benzoyl*-N^1-*acetylsulphanilamide*, m.p. 262—263°, is obtained from the *N*^{4}-Bz derivative, m.p. 285—286° (lit. 280°), by Ac_2O–C_5H_5N at 100° and from the *N*^{1}-Ac derivative by BzCl–C_5H_5N at 100°. The *N*^{1}*N*^{4}-Bz_2 derivative, m.p. 260° (decomp.) (cf. lit.), is also prepared. R. S. C.

Substituted phenols.—See B., 1944, II, 222.

Reaction of phenols with *tert.*-butyl chloride. S. C. Burket and R. Q. Brewster (*Trans. Kansas Acad. Sci.*, 1943, **46**, 133—135).—$Bu^{\gamma}Cl$ and various *o-* and *p*-C_6H_4R·OH either do not react (in presence of C_5H_5N and, occasionally, $CaCO_3$) or give CMe_2:CH_2 and unchanged phenol (with NaOEt or $CaCO_3$). 5 : 2 : 1-C_6H_3MeCl·OH, *p*-CMe_2Et·C_6H_4·OH, and *p*-$C_6H_4Bu^{\gamma}$·OH (using $CaCO_3$) give their *Bu*$^{\gamma}$ *ethers*, b.p. 265—270°/740 mm., 270—275°/740 mm., and 255—260°/740 mm., respectively. M. H. M. A.

Phenylcarbamyl derivatives of alkylated phenols. M.p. and *X*-ray powder diffraction data. J. B. McKinley, J. E. Nickels, and S. S. Sidhu (*Ind. Eng. Chem.* [*Anal.*], 1944, **16**, 304—308).—*Phenylurethanes* of the following phenols are prepared: *p*-chloro-, m.p. 148·5°, *p*-nitro-, m.p. 156°, 4-chloro-2-*tert.*-butyl-, m.p. 133°, *p-tert.*-butyl-, m.p. 148·5°, 4-methyl-2-β-methylallyl-, m.p. 98·5°, *p-tert.*-amyl-, m.p. 108°, 2-methyl-4(or 6)-*tert.*-butyl-, m.p. 139·5°, 2-methyl-6(or 4)-*tert.*-butyl-, m.p. 189°, 3-methyl-4(or 6)-*tert.*-butyl-, m.p. 133°, 4-methyl-2-*tert.*-butyl-, m.p. 155°, *p*-phenyl-, m.p. 167·5°, *o-*, m.p. 111·5°, and *p-*, m.p. 145·5°, *-cyclo*hexyl-, 4-methyl-2-*tert.*-amyl-, m.p. 124°, 3-ethyl-4(or 6)-*tert.*-butyl-, m.p. 156°, 4-ethyl-2-*tert.*-butyl-, m.p. 134°, 2 : 3-dimethyl-4(or 6)-*tert.*-butyl-, m.p. 216°, 2 : 4-dimethyl-6-*tert.*-butyl-, m.p. 173°, 2 : 5-dimethyl-4-*tert.*-butyl-, m.p. 144°, 2 : 6-dimethyl-4-*tert.*-butyl-, m.p. 160°, 3 : 4-dimethyl-6-*tert.*-butyl-, m.p. 142°, 3 : 5-dimethyl-2 : 6-diethyl-, m.p. 226°, 2-methyl-3 : 5-di*iso*propyl-, m.p. 198·5°, 4-methyl-3 : 5-di*iso*propyl-, m.p. 256°, 2-methyl-4 : 6-di*tert.*-butyl-, m.p. 163·5°, 3-methyl-4 : 6-di*tert.*-butyl-, m.p. 171·5°, 4-*cyclo*hexyl-2-*tert.*-butyl-, m.p. 170°, 3-ethyl-4 : 6-di*tert.*-butyl-, m.p. 182·5°, 2 : 3-dimethyl-4 : 6-di*tert.*-butyl-phenol, m.p. 216°. *X*-Ray diffraction data (interplanar spacing) are presented for all the above, and also for the phenylurethanes of PhOH, PhSH, *o-*, *m-*, and *p*-cresol, *o-*, *m-*, and *p*-ethyl-, 2 : 3-, 2 : 4-, 2 : 5-, 3 : 4-, and 3 : 5-dimethyl-, and 2 : 4 : 6-trimethylphenol. J. D. R.

***p*-Bromoaniline salts of monoaryl sulphates.** D. H. Laughland and L. Young (*J. Amer. Chem. Soc.*, 1944, **66**, 657—658).—$KArSO_4$ with *p*-C_6H_4Br·NH_2,HCl in H_2O give p-C_6H_4Br·NH_2 *Ph*, o-*anisyl*, p-C_6H_4Br, p-*tolyl*, and α-$C_{10}H_7$ *sulphate*, which are unstable and have ill-defined m.p. R. S. C.

Dialkylstilbœstrols.—See B., 1944, III, 142.

Synthesis of two dihydroxyterphenyls. C. C. Price and G. P. Mueller (*J. Amer. Chem. Soc.*, 1944, **66**, 632—634).—Dropping *o*-$C_6H_4(C_6H_4$·N_2Cl-*p*$)_2$ in H_2O into boiling H_2O–steam gives 4 : 4″-*dihydroxy*-o-*terphenyl* (98%), m.p. 230·2—231·2° (corr.) [*diacetate*, m.p. 186—186·4° (corr.); *Me*$_2$ *ether*, m.p. 104·8—106·4° (corr.)]. *p*-$C_6H_4(C_6H_4$·NO_2-*p*$)_2$ with H_2–Raney Ni in C_6H_6 at 100°/2000 lb. gives the $(NH_2)_2$-compound, m.p. 240—244° [dihydrochloride, darkens 315°, m.p. 355—370° (decomp.)], whence 4 : 4″-*dihydroxy*-p-*terphenyl* (I), m.p. 375° [*diacetate*, m.p. 244·3—245·3° (corr.); *Me*$_2$ *ether* (II), m.p. 273—275°], is obtained as above but in very poor yield. *p*-OMe·C_6H_4·MgBr (III) and 1 : 2-dibromo*cyclo*hexane in Et_2O and later boiling Bu_2O give (II), and 4 : 4″-*dimethoxydiphenyl* (IV), m.p. 174·5—175·6°. Hydrolysis of (II) to (I) by KOH–EtOH at 200° and then oxidation by $KMnO_4$–NaOH gives

p-$C_6H_4(CO_2H)_2$ (proof of structure). (**III**) and (**IV**) in Bu_2O and then at 140° give a small amount of (**II**) and homologues. R. S. C.

Selective hydrogenation of eugenol and *iso*eugenol in presence of Raney nickel. B. Gauthier (*Compt. rend.*, 1943, **217**, 28—30).—Eugenol (**I**) and H_2–Raney Ni at room temp. yield *dihydroeugenol* (**II**), b.p. 133—135°/19 mm. (*formate*, b.p. 140°/12 mm.; *acetate*, b.p. 149—150°/14 mm.; *propionate*, b.p. 154—155°/12 mm.; *isobutyrate*, b.p. 158°/15 mm.; *butyrate*, b.p. 164°/13 mm.; *isovalerate*, b.p. 170°/13 mm.; *p-nitrobenzoate*, m.p. 76°; *cinnamate*, m.p. 88°; *phenylurethane*, m.p. 122°; *diphenylylurethane*, m.p. 104—105°); at 60—65°, hydrogenation yields (**II**) and a little octahydroeugenol. *iso*Eugenol is hydrogenated (as above) only slowly at 20°. EtOH accelerates hydrogenation in both cases [(**I**) > (**II**)]. A. T. P.

Condensation of vanillin substitution products with nitromethane. L. C. Raiford and D. E. Fox (*J. Org. Chem.*, 1944, **9**, 170—174).—β-Nitrostyrenes are best obtained by gently boiling a solution of vanillin or its substitution products and $MeNO_2$ in AcOH containing NH_4OAc, less frequently by keeping a solution of these reactants in abs. EtOH at room temp. for several days. *β-Nitro-3:4-dimethoxystyrene*, m.p. 140—141°, and the 2-, m.p. 134—135°, 5-, m.p. 190—191°, and 6-*Br*-, m.p. 168—169°, 5:6-Br_2-, m.p. 166—167°, 2-, m.p. 188—189°, and 5-NO_2-, m.p. 183—184°, and 5-*bromo-2-nitro*-, m.p. 169—170°, -derivatives of β-nitro-4-hydroxy-3-methoxystyrene are described. Treatment of these compounds with Br saturates the side-chain and introduces Br at $C_{(5)}$ if OH is attached to $C_{(4)}$, thus giving *αβ-dibromo-β-nitro-α-p-bromo-4-hydroxy-3-methoxyphenylethane* (**I**), m.p. 127°, -α-5:6-*dibromo-4-hydroxy-3-methoxyphenylethane* (**II**), m.p. 126—128° after softening, and -α-3:4-*dimethoxyphenylethane* (**III**), m.p. 113—114° (+0·5CS_2) (lost at ~65°/1 hr.). (**I**) is transformed by repeated crystallisation from EtOH or by boiling EtOH containing NaOAc into *β:5-dibromo-β-nitro-4-hydroxy-3-methoxystyrene*, m.p. 166—167°, whilst (**II**) under similar conditions gives *β:5:6-tribromo-β-nitro-4-hydroxy-3-methoxystyrene*, m.p. 175—176°. At room temp. NaOAc in EtOH transforms (**III**) into *β-bromo-β-nitro-3:4-dimethoxystyrene*, m.p. 119—120°. Oxidation of the condensation products or their Br adducts with $KMnO_4$ causes loss of Br from the side-chain and gives the related aldehyde. When veratraldehyde is used as initial material, oxidation of the condensation product gives the related acid, thus emphasising the retarding effect of *p*-OH. H. W.

Condensation of *cyclo*hexene oxide, 1:2-dichloro*cyclo*hexane, and γδ-dichlorohexane with anisole. C. C. Price and G. P. Mueller (*J. Amer. Chem. Soc.*, 1944, **66**, 628—631).—Passing BF_3 into *cyclo*hexene oxide (**I**) and PhOMe at 40—70° gives *trans*-1:2-dihydroxy-*cyclo*hexane (**II**) and a little *p-cyclo*hexylphenol (3:5-*dinitrobenzoate*, m.p. 164—166°). Passing BF_3 into (**I**) and PhOMe at 50° gives *p-cyclo*hexylanisole (**III**) (8%), 1:3-*di*-p-*anisyl*cyclo*hexane* (**IV**), *form*, b.p. 160—165°/1 mm., and m-*di*-p-*anisylbenzene* [4:4″-*dimethoxy*-m-*terphenyl*] (**V**), m.p. 197—198° (corr.), also obtained in poorer yield from (**II**). Similar products are obtained from 1:2-dichloro*cyclo*hexane and PhOMe by $AlCl_3$ at 5°, but an *isomeride* (**VI**), m.p. 102·8—104°, of (**IV**) is also obtained. Formation of (**III**), (**IV**), and (**V**) probably results by disproportionation of 3-*p*-anisyl-Δ¹-*cyclo*hexene. 10% Pd–C at 300° converts (**IV**) or (**VI**) into (**V**). KOH–EtOH at 200° converts (**VI**) into 1:3-*di*-p-*hydroxyphenyl*cyclo*hexane* (**VII**) (97%), m.p. 229—232° (*diacetate*, m.p. 74·5—75·5°), but (**IV**) gives an oil. With KOH–EtOH at 200° or HI–AcOH, (**V**) gives 4:4″-*dihydroxy*-m-*terphenyl* (**VIII**), m.p. 182—183° (*diacetate*, m.p. 130·1—131·5°), but KOH–EtOH occasionally yields a *substance*, $C_{20}H_{36}O_2$, +0·5EtOH, m.p. 66—67·5°. $KMnO_4$–NaOH oxidises (**VIII**) to *m*-$C_6H_4(CO_2H)_2$. Pd–C and a trace of Zn dust at 250° convert (**VII**) into *m*-$C_6H_4Ph_2$. $(CHEtCl)_2$ with PhOMe and $AlCl_3$ in light petroleum at the b.p. and then Me_2SO_4–20% aq. NaOH gives 1% of hexœstrol Me_2 ether, m.p. 142—143° (corr.). (**VII**) and (**VIII**) have no œstrogenic and (**VII**) has no androgenic activity. R. S. C.

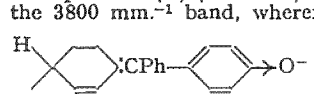
Absorption spectra of 1:2-benzenthracene and some methoxy-derivatives.—See A., 1944, I, 164.

Syntheses of compounds related to vitamin-*K*. II. 4′-Hydroxy-3-alkylnaphthalene-1′-azobenzene-4-sulphonamides. E. J. H. Chu, Z. I. Shen, T. L. Chien, and T. S. Tuan (*J. Amer. Chem. Soc.*, 1944, **66**, 653).—α-$C_{10}H_7$·O·COR with $ZnCl_2$ or $SnCl_4$ at 140—150° gives good yields of 1:2-OH·$C_{10}H_6$·COR (formed also in minor amounts by $AlCl_3$). 2:1-$C_{10}H_6$Alk·OH and *p*-NH_2·SO_2·C_6H_4·N_2X in aq. AcOH give *4′-hydroxy-3′-ethyl*- (73%), m.p. 249°, -n-*propyl*- (69%), m.p. 251°, -n- (66%), m.p. 280°, and -*iso*-butyl-, a gum, -n-*amyl*- (56%), m.p. 260°, and -*β-phenylethyl*- (51%), m.p. 261°, -*naphthalene-1′-azobenzene-4-sulphonamide*, which have no inhibitory effect on growth of *B. coli*, *Staph. aureus*, or *Strept. pyogenes*. 2:1-Ph·$[CH_2]_2$·$C_{10}H_6$·OH has m.p. 77—78° (decomp.) and gives a *picrate*, m.p. 179—180° (decomp.). 1:2-OH·$C_{10}H_6$·COR (R = $Pr^β$ and Bu^n; not Me) are obtained from the 1:4-isomerides by boiling 35% NaOH. R. S. C.

Aralkyl iodides and alcohols.—See B., 1944, II, 221.

Rearrangement of β-amino-alcohols with heat and alkali. B. K. Campbell and K. N. Campbell (*J. Org. Chem.*, 1944, **9**, 178—183).—Three aryl-substituted β-NH_2-alcohols rearrange to ketimines under the influence of heat and CaO; the change is shown to occur probably through the corresponding ethyleneimines. β-Amino-*aa*-diphenylpropan-α-ol is converted by CaO under N_2 at 270° into CPh_2:NEt (**I**), b.p. 154—159°/10 mm., m.p. 58—59°; at 130—230° the amine is scarcely affected. (**I**) is readily hydrolysed by 6N-HCl at room temp. to $COPh_2$ and NH_2Et, and is reduced by Na and abs. EtOH to $CHPh_2$·$NHEt$ (**II**), b.p. 142°/8 mm. (**I**) is obtained by passing dry NH_2Et over CPh_2:NPh and a little NH_2Ph,HBr at 230°, and (**II**) from MgPhBr and CHPh:NEt. 2:2-Diphenyl-3-methylethyleneimine is transformed into (**I**) in presence of CaO at 250—260° or in its absence at 175—205°. β-Amino-α-phenyl-α-*p*-tolylethanol and CaO at 260° afford *Ph* p-*tolyl ketmethylimine*, b.p. 165—169°/13 mm., also obtained from NPh:CPh·C_6H_4Me-*p*, NH_2Ph,HBr, and dry NH_2Me at 200—210°; it is readily hydrolysed to COPh·C_6H_4Me-*p* and NH_2Me. It is reduced by Na and abs. EtOH to N:p-*dimethylbenzhydrylamine*, b.p. 169—172°/16 mm. [hydrochloride, m.p. 186—187° (lit. 199—201°); α-*naphthylcarbamyl* derivative, m.p. 171·5—172·5°], also obtained from CHPh:NMe and *p*-C_6H_4Me·MgBr. NH_2·CHPh·CPh_2·OH is partly rearranged by CaO at 260° to CPh_2:N·CH_2Ph, hydrolysed to $COPh_2$ and CH_2Ph·NH_2. H. W.

Quinoidation of triaryl compounds: (A) hydroxyphenyldiphenylylcarbinols, (B) hydroxydiphenylyldiarylmethyl cations. L. C. Anderson and W. A. Fisher (*J. Amer. Chem. Soc.*, 1944, **66**, 589—593, 594—597).—(A) Introduction of 1 or 2 *p*-C_6H_4Ph into *p*-OH·C_6H_4·CAr_2·OH (*A*) causes a high and broad absorption band at ~3800 mm.$^{-1}$, similar to that of Ph_2 and due to C_6H_4Ph; this band covers the benzenoid absorption of (*A*) (Ar = Ph). Diphenylquinomethanes do not give the 3800 mm.$^{-1}$ band, wherefore it is concluded that the C_6H_4Ph structure is different and that absorption of fuchsones in Et_2O is due largely to a structure (*B*).



(*B.*)

p-C_6H_4Ph·CPhCl$_2$ (**I**) and PhOH at room temp. give *p*-OH·C_6H_4·$CPh(C_6H_4Ph$-*p*$)$·OH (**II**) (*acetate*, m.p. 134—136°) contaminated with *p*-C_6H_4Ph·COPh and $(p$-OH·$C_6H_4)_2$CPh·C_6H_4Ph-*p*. At 130—140°/vac. (**II**) is dehydrated to *phenyl*-p-*diphenylylquinomethane* (**III**), m.p. 166—167°, whence warm 70% AcOH yields the quinonoid form (**IV**), m.p. 139—140°, of (**II**). Passing CO_2 into a solution of (**III**) or (**IV**) in 2·5% NaOH gives the benzenoid form, m.p. 155—157°, of (**II**). $AlCl_3$ in boiling C_6H_6 converts the Me ether of (**II**) into (**IV**), m.p. 134—140°. PhOH and (**I**) in boiling dry C_6H_6 (1 hr.) give *diphenoxyphenyl*-p-*diphenylylmethane*, m.p. 149—150°, but PhOH and (**I**) alone at 100° (5 days) give 4:4′-*dihydroxytriphenyl*-p-*diphenylylmethane* (55%), softens 157°, m.p. 163—165° (*diacetate*, m.p. 168—170°, clear at 187°). By similar reactions $(p$-$C_6H_4Ph)_2CCl_2$ [prep. from $CO(C_6H_4Ph$-*p*$)_2$ by PCl_5] gives *p-hydroxyphenylbisdiphenylylcarbinol*, quinonoid, m.p. 106—107·5°, and benzenoid forms, m.p. 124—126° (*acetate*, m.p. 149—152°), *bis*-p-*diphenylylquinomethane*, m.p. 140—155° (slow heating) or 159—161·5° (bath preheated at 150°), *diphenoxybis*-p-*diphenylylmethane*, m.p. 118—120°, and di-*p*-hydroxyphenylbis-*p*-diphenylylmethane, m.p. 253—255·5° (*diacetate*, m.p. 256—258°).

(B) Absorption spectra are recorded for *b-p′*-OR·C_6H_4·C_6H_4·$CArAr′$·OH (*C*) (R = H or OMe; Ar and Ar′ = Ph or *p*-C_6H_4Ph) in AcOH–H_2SO_4. Comparison with the spectra of *p*-C_6H_4Ph·CPh_2·OH and *p*-C_6H_4Ph·$CPh(C_6H_4$·OMe-*p*$)$·OH (**V**) indicates that C_6H_4Ph is quinonoid when R in (*C*) is Me. (*C*) (Ar = Ar′ = Ph; R = H) does not exist in a quinonoid form and gives no diphenyldiphenylylquinomethane. (**V**) is prepared from *p*-OMe·C_6H_4·MgBr (**VI**) and *p*-C_6H_4Ph·COPh and from the phenol by Me_2SO_4. $CO(C_6H_4Ph$-*p*$)_2$ and (**VI**) in boiling Et_2O–C_6H_6 give p-*anisylbis*-p-*diphenylylcarbinol*, m.p. 146°. *p*-OH·C_6H_4·C_6H_4·COPh-*p* and MgPhBr in boiling C_6H_6–Et_2O give *diphenyl-4′-hydroxy-p-diphenylylcarbinol*, m.p. 224—227° (*acetate*, m.p. 154—156·5°), which is also obtained by $AlCl_3$–C_6H_6 from its *Me ether*, m.p. 108—109° (prep. from *p*-OMe·C_6H_4·C_6H_4·COPh-*p* by MgPhBr). *p*-C_6H_4Ph·COCl (prep. from the acid by $SOCl_2$), *p*-C_6H_4Ph·OMe, and $AlCl_3$ in $(CHCl_2)_2$ at −10° to room temp. give p-C_6H_4Ph *4′-methoxy-p-diphenylyl ketone* (**VII**) (50—65%), m.p. 246—248°, with 10—25% of p-*C*$_6H_4Ph$ *6-methoxy-3-diphenylyl ketone*, m.p. 127—130°. MgPhBr and (**VII**) in boiling Et_2O give *phenyl*-p-*diphenylyl-4′-methoxy*-p-*diphenylylcarbinol*, m.p. 141—143°. *p*-OMe·C_6H_4·C_6H_4·CO_2H-*p*′ (prep. from the *p′*-COMe compound by $KMnO_4$ or NaOI) gives, best in a Soxhlet apparatus over H_2SO_4–MeOH, its Me ester, which with an excess of *p*-C_6H_4Ph·MgBr gives *bis*-p-*diphenylyl-4′-methoxy*-p-*diphenylylcarbinol*, m.p. 130—132°. R. S. C.

Reductions with nickel–aluminium alloy and aqueous alkali. IV. Carbon–carbon double linking. E. Schwenk, D. Papa, B. Whitman, and H. F. Ginsberg (*J. Org. Chem.*, 1944, **9**, 175—177).—Examples of the reduction of conjugated, isolated, and cyclic double linkings using Ni–Al alloy and aq. alkali are afforded by CHPh:CH·CO_2H, maleic, crotonic, oleic, and sorbic acid, *p*-OH·C_6H_4·CH:CHPh, *b*-OH·C_6H_4·CH:CPh·CO_2H, *p*-OMe·C_6H_4·CH:CPh·CO_2H, CHPh:C$(C_6H_4$·OMe$)$·CO_2H, CHPh:C$(C_6H_4$·OH$)$·CO_2H, *cyclo*hexyl-

ideneacetic (**I**), α-Δ¹-*cyclo*hexenyl- and *p*-hydroxy-Δ¹-*cyclo*hexenylcinnamic acid. Δ⁵-3(β)-Hydroxyætiocholenic acid is recovered unchanged and the reduction of Δ¹-*cyclo*hexenylacetic acid is so incomplete as to suggest a preliminary partial isomerisation to (**I**). The *cyclo*pentene ring of chaulmoogric acid is quantitatively reduced. Stilbœstrol gives the hexœstrols, m.p. 184—185° and 126—128°, in 30 and 50% yield respectively. The following appear new: α-*phenyl*-β-p-*anisylpropionic acid*, m.p. 119—120°; β-*phenyl*-α-p-*anisylpropionic acid*, m.p. 108—109°; β-*phenyl*-α-p-*hydroxyphenylpropionic acid*, m.p. 158—159°; α-p-*hydroxyphenylcinnamic acid*, m.p. 221—222°; α-cyclo*hexyl*-β-*phenyl*-, m.p. 70—71°, and -β-p-*hydroxyphenyl*-, m.p. 180—181°, -*propionic acid*. α-*p*-Anisylcinnamic acid has m.p. 152—153° (lit. 132—133°). H. W.

Steroids and sex hormones. XCVIII. Preparation of β-*trans*-4-hydroxy*cyclo*hexyl-Δ^αβ^-butenolide. E. Hardegger, P. A. Plattner, and F. Blank (*Helv. Chim. Acta*, 1944, **27**, 793—800).—$CNa_2(CO_2Et)_2$ and $CH_2Cl{\cdot}CH_2{\cdot}CO_2Et$ give *Et*$_4$ *pentane-αγγε-tetracarboxylate* (**I**), b.p. 157—160°/high vac., cyclised by Na to *Et*$_3$ cyclo*hexanone*-2 : 4 : 4-*tricarboxylate* (**II**), b.p. 187—189°/water pump vac., with some *Et* cyclo*hexanone*-4-*carboxylate*, b.p. 137°/water pump vac. (**II**) in C_6H_6 is hydrolysed by aq. NaOH at room temp. to cyclo*hexanone*-4 : 4-*dicarboxylic acid*, m.p. 147·5—149·5°. (**I**) is converted by successive treatment with Na, EtOH, and C_6H_6 at 100° followed by hydrolysis into cyclo*hexanone*-4-*carboxylic acid* (**III**), m.p. 67—68°, which is reduced (H_2, Raney Ni, N-NaOH) to cis-4-*hydroxyhexahydrobenzoic acid*, m.p. 150·5—151° (*Me* ester), converted by boiling Ac_2O into the lactone, m.p. 128° (lit. 109—110°). Na–Hg, or (less well) H_2–PtO_2–AcOH, reduces (**III**) to *trans*-4-hydroxyhexahydrobenzoic acid, m.p. 119—120° (*Me* ester and its *benzoate*, m.p. 92—94°). This is converted by boiling AcCl–Ac_2O–AcOH into trans-4-*acetoxyhexahydrobenzoic acid*, m.p. 139—140° (*Me* ester, m.p. 45·5—46·5°), and thence ($SOCl_2$) into the chloride and *diazoketone*, decomp. 86—87°, which passes in AcOH at 100° into trans-4-*acetoxy*cyclo*hexyl OAc·CH*$_2$ *ketone* (**IV**), m.p. 67—68° (*semicarbazone*, m.p. 167—168°). (**IV**) is readily transformed by Zn and $CH_2Br{\cdot}CO_2Et$ followed by acetylation into β-*acetoxy*-β-trans-4-*acetoxy*cyclo*hexylbutyrolactone*, m.p. 142—142·5°, which passes at 225—240°/water pump vac. into β-trans-4-*acetoxy*cyclo*hexyl*-Δ^αβ^-*butenolide*, m.p. 88—89°, giving a positive Legal test. β-trans-4-*Hydroxy*cyclo*hexyl*-Δ^αβ^-*butenolide* has m.p. 95—95·5°. H. W.

Synthetic anthelmintics. IX. γ-6-Methoxy-*m*-tolyl- and γ-*p*-anisyl-α-alkylbutyrolactones. S. V. Mehta, J. J. Trivedi, K. V. Bokil, and K. S. Nargund (*J. Univ. Bombay*, 1944, **12**, **A**, Part 5, 33—35).—The appropriate alkylsuccinic anhydride and *o*-$C_6H_4Me{\cdot}OMe$ (Friedel–Crafts) give γ-*keto*-γ-6-*methoxy*-m-*tolyl*-α-*ethyl*-, m.p. 99° (*semicarbazone*, m.p. 179°), -α-n-*propyl*-, m.p. 96—97° (*semicarbazone*, m.p. 159°), and -α-n-*amyl-butyric acid*, m.p. 40—45° (purified through its *Et* ester, b.p. 260—265°/60 mm.), converted (method: A., 1942, II, 257) into γ-6-*methoxy*-m-*tolyl*-α-*ethyl*-, m.p. 63—64°, -α-n-*propyl*-, m.p. 93°, and -α-n-*amyl-butyrolactone*, m.p. 38—39°, b.p. 258°/28 mm., respectively. Similarly prepared from *p*-$OMe{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2{\cdot}CHAlk{\cdot}CO_2H$ (A., 1944, II, 78) are γ-p-*anisyl*-α-*ethyl*-, m.p. 91—92°, -α-n-*propyl*-, m.p. 98—99°, -α-n-*amyl*-, m.p. 92°, -α-n-*hexyl*-, m.p. 98°, -α-n-*tetradecyl*-, m.p. 79—80°, and -α-n-*hexadecyl-butyrolactone*, m.p. 95—96°. A. T. P.

Action of diazobenzene on alkylacetoacetic esters as a method of preparing phenylhydrazones of α-keto- and α-amino-acids. VIII. Synthesis of tyrosine. V. V. Feofilaktov, V. N. Zaitzeva, and K. I. Sirotkina (*J. Gen. Chem. Russ.*, 1943, **13**, 363—372).—Methods of synthesis of tyrosine are reviewed and a new procedure is described. To a stirred mixture of $CH_2Ac{\cdot}CO_2Et$ (10% excess) and NaOEt in EtOH at room temp., *p*-$OMe{\cdot}C_6H_4{\cdot}CH_2Cl$ (prep. from PhOMe, CH_2O, and HCl in presence of $ZnCl_2$) was added dropwise, and the mixture then heated at 100° (bath) for 3 hr.; the resulting *Et* α-p-*methoxybenzylacetoacetate* (76·2%), b.p. 160—161°/3 mm., was added gradually with vigorous stirring to an equiv. of aq. $PhN_2{\cdot}OK$ and, after an additional 4 hr. stirring, the product extracted with Et_2O. Hydrolysis (aq. EtOH–KOH) of the Et_2O-sol. ester gives p-*anisylpyruvic acid phenylhydrazone* (**I**) (75·3%), dimorphic from C_6H_6–ligroin (b.p. 90—94°) (1 : 1), less sol. α-form, platelets, m.p. 158—159°, and predominating β-form, needles, m.p. 150°. (**I**) (crude or once crystallised) was reduced with Zn dust and HCl–EtOH, the EtOH evaporated in a vac., the residue ground with Ag_2CO_3, and then extracted with boiling H_2O. The aq. extracts, freed from metals with H_2S, were evaporated and crystallised from H_2O to give 55—58% of *p*-$OMe{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H$ (**II**), m.p. 262° (sealed tube). (**II**) with boiling HI (b.p. 126°) for 5 hr. gives tyrosine (95·6%). R. C. P.

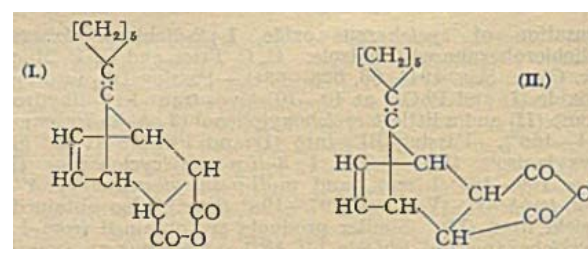
Raman spectra of salicylic acid and aspirin.—See A., 1944, I, 165.

Nitro- and nitroamino-derivatives of *o*-chlorobenzoic acid. H. Goldstein and G. Preitner (*Helv. Chim. Acta*, 1944, **27**, 612—615; cf. A., 1938, II, 13, 98).—6 : 2 : 5 : 1-$NO_2{\cdot}C_6H_2Cl(NH_2){\cdot}CO_2H$ in EtOH–conc. H_2SO_4 is converted by *iso*-$C_5H_{11}{\cdot}O{\cdot}NO$ at −10°, followed by a little Zn dust at the b.p., into 6 : 2 : 1-$NO_2{\cdot}C_6H_2Cl{\cdot}CO_2H$ (**I**), also obtained by oxidising 1 : 2 : 6-$C_6H_3MeCl{\cdot}NO_2$; lower yields of very impure product are obtained by diazotisation in H_2O and adding EtOH. The chloride ($SOCl_2$) of (**I**) yields the Me, m.p. 94—95 (lit. 80—82°), and *Et* ester, m.p. 49—50°, the *amide*, m.p. 186—187°, and *anilide*, m.p. 176—177°. 1 : 2 : 5-$C_6H_3MeCl{\cdot}NHAc$ and HNO_3 (*d* 1·4 mixed with *d* 1·52) at ⩾15° give a mixture of mainly 2-chloro-4-nitro- (**II**), m.p. 113°, and a little 2-*chloro*-6-*nitro*-5-*acetamidotoluene* (**III**), m.p. 152—153°; the proportion of (**III**) is increased by using HNO_2 (*d* 1·52) in AcOH at 5—10°. (**II**) is oxidised (aq. $KMnO_4 + MgSO_4$) to 2-*chloro*-4-*nitro*-5-*acetamidobenzoic acid*, m.p. 214°, hydrolysed by boiling dil. HCl to the 5-NH_2-*acid*, m.p. 239—240° (decomp.). Similarly (**III**) gives 6 : 2 : 5 : 1-$NO_2{\cdot}C_6H_2Cl(NHAc){\cdot}CO_2H$. M.p. are corr. H. W.

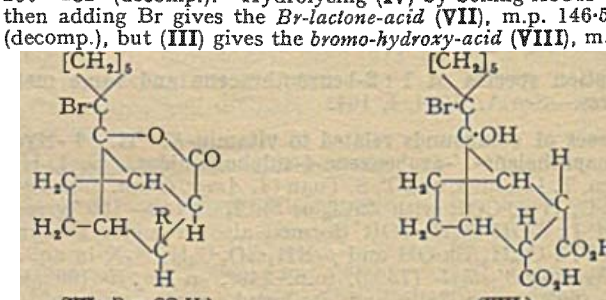
***N*-Substituted piperonylamides.** S. I. Gertler and W. F. Barthel (*J. Amer. Chem. Soc.*, 1944, **66**, 659—660).—*Piperonyl-ethyl*-, m.p. 87—88°, -n-*propyl*-, m.p. 86—87°, and -n-*amyl-amide*, m.p. 104—105°, -m-*chloro*-, m.p. 110·5—112·5°, -o-, m.p. 109·5—110°, -m-, m.p. 116—117°, and -p-*bromo-anilide*, m.p. 222—222·5°, are prepared. M.p. are corr. R. S. C.

Attempted syntheses of hemipinic acid from guaiacol. C. Weizmann and L. Haskelberg (*J. Org. Chem.*, 1944, **9**, 121—124).—2 : 3 : 1-$OH{\cdot}C_6H_3(OMe){\cdot}CO_2H$, m.p. 200°, is obtained in good yield from dry *o*-$ONa{\cdot}C_6H_4{\cdot}OMe$ and CO_2 at 200° whereas at 230° it is accompanied by 2 : 3 : 1 : 4-$(OH)_2C_6H_2(CO_2H)_2$, m.p. 308°. With Br in AcOH or $CHCl_3$ at room temp. it affords 5-*bromo*-2-*hydroxy*-3-*methoxybenzoic acid*, m.p. 211° [*Me* ester, m.p. 122° (*acetate*, m.p. 95°), obtained similarly from 2 : 3 : 1-$OH{\cdot}C_6H_3(OMe){\cdot}CO_2Me$]. Bromination of 3 : 2 : 1-$OMe{\cdot}C_6H_3(OAc){\cdot}CO_2Me$ in AcOH containing anhyd. NaOAc, in $CHCl_3$, or without solvent leads to *Me* 6-*bromo*-3-*methoxy*-2-*acetoxybenzoate*, m.p. 124°, hydrolysed (aq. EtOH–NaOH) to 6-*bromo*-2-*hydroxy*-3-*methoxybenzoic acid*, m.p. 150°, which with NaCN and CuCN in 50% EtOH at 180° gives *iso*vanillic acid, also obtained from 5-bromoguaiacol, NaCN, and CuCN under the same conditions. H. W.

Diene-addition reactions. II. Reaction of 6 : 6-pentamethylenefulvene with maleic anhydride. R. B. Woodward and H. Baer (*J. Amer. Chem. Soc.*, 1944, **66**, 645—649; cf. A., 1943, II, 119).—6 : 6-Pentamethylenefulvene and $(CH{\cdot}CO)_2O$ in C_6H_6 at 5° give the endo- (**I**), m.p. 132°, and some of the exo-*adduct* (**II**), $C_{15}H_{14}O_3$, m.p. 93·0—93·5°, but at higher temp. more and more (**II**) is obtained (cf. Alder *et al.*, A., 1937, II, 321; Kohler *et al.*, A., 1935, 852). H_2–PtO_2 in EtOH reduces the *cyclo*hexene CH:CH of (**I**) or



(**II**) to give the endo- (**III**), m.p. 146°, and exo-H_2-*adducts* (**IV**), m.p. 103—104°, respectively; resistance of the *cyclo*hexylidene C:C accords with the views of Linstead *et al.* (A., 1943, II, 62). Dissolving (**III**) or (**IV**) in MeOH and adding 10% aq. NaOH until alkaline to phenolphthalein gives the *Me H* endo-, m.p. 114° (Et H ester, m.p. 104·5—105°), or exo-H_2-ester, m.p. 118°, and thence the Me_2 endo- (**V**), a gum, and exo-H_2-ester (**VI**), m.p. 65°, respectively. (**II**) and EtOH similarly give the corresponding *Et H* ester, m.p. 137—137·5°. (**V**) and (**VI**) are both *cis*-esters, for both are isomerised by NaOMe–MeOH at the b.p. to the trans-Me_2 H_2-ester, m.p. 75°, whence HCl–AcOH yields the trans-*dicarboxylic acid*, m.p. 230—232° (decomp.). Hydrolysing (**IV**) by boiling AcOH–H_2O and then adding Br gives the *Br-lactone-acid* (**VII**), m.p. 146·5—147·5° (decomp.), but (**III**) gives the *bromo-hydroxy-acid* (**VIII**), m.p. 152—



153° (decomp.), this difference proving the stereochemical configurations. (**I**) dissociates in, *e.g.*, EtOAc or C_6H_6, slowly when cold and rapidly when heated, but (**II**) is stable, which accounts for the variation (above) in the ratio (**I**) : (**II**) produced. The modes of addition and the differences are discussed on electronic and energetic grounds. R. S. C.

9-Acylfluorenes and derived vinylamines. I. Von and E. C. Wagner (*J. Org. Chem.*, 1944, **9**, 155—169).—The formation of 9-

acylfluorenes by alkali-induced condensation of esters with the reactive CH_2 of fluorene (I) has been extended to the 9-Ac compound. Fluorene-9-aldehyde (II) is obtained by similar use of 1-formylpiperidine, showing the ability of the latter to function as an aquo-ammono-ester of HCO_2H. The attempted ester condensation (for the prep. of CHO-derivatives) gives tarry products when applied to *cyclo*pentadiene and indene whilst reaction does not occur with xanthene or acridan. The products from (I) and its 2 : 7-Br_2-derivative and NH_3 are shown to be enamines and di-9-fluorenylmethyleneamines. (II), b.p. 169—172°/2 mm. [prep. from (I), KOMe, and HCO_2Et or, less well, by use of Na, NaOMe, or CPh_3Na], polymerises when kept. 2 : 7-Dibromofluorene-9-aldehyde, m.p. 180—181° (corr.), is converted by BzCl and NaOH into the enol *benzoate*, m.p. 221° (corr.), and by NH_2Ph in EtOH into the *anil*, m.p. 226—227° (corr.). 9-*Acetylfluorene*, m.p. 74·5—75·5° (corr.), obtained from (I), KOMe, and EtOAc in anhyd. Et_2O, gives a somewhat unstable *phenylhydrazone*, m.p. 138—139° (corr.; decomp.), and an apparently stable *oxime*, m.p. 137° (corr.); it liquefies when kept in a desiccator at room temp. and then solidifies to the *dimeride*, m.p. 247—248° (corr.), which does not react with NHPh·NH_2. It does not condense with NH_2Ph or piperidine in dry C_6H_6 at 100°. Passage of dry NH_3 into a solution of (II) in dry C_6H_6 or Et_2O at 0° leads to 9-aminomethylenefluorene (III), m.p. 146—147° after softening, with a smaller proportion of di-9-fluorenylmethyleneamine (IV). (III) becomes discoloured when kept in a desiccator, immediately reduces $KMnO_4$, is indifferent to 10% NaOH at 100°, is immediately converted into (IV) by acid, and is monomeric in freezing C_6H_6. With dry HCl in Et_2O it yields the hydrochloride, chars without melting ~300°. (III) and Ac_2O in a vac. over NaOH and $CaCl_2$ afford 9-*acetamidomethylenefluorene*, m.p. 204·5—206° (corr.), which could not be cyclised to the *iso*quinoline derivative by P_2O_5 in PhMe. Ozonolysis of (III) in $CHCl_3$ and treatment of the ozonide with H_2O at 100° gives fluorenone (V) and HCO·NH_2 (identified by conversion by *o*-NH_2·C_6H_4·CO_2H into 3 : 4-dihydro-4-quinazolone, m.p. 212—213°). (III) is transformed by Br in $CHCl_3$ followed by H_2O into NH_4Br and 9-bromofluorene-9-aldehyde (VI). (IV) is obtained synthetically from (II) and (III) in C_6H_6. Ozonolysis of (IV) gives (V) and diformamide and brominolysis yields (VI). Not quite homogeneous 2 : 7-*dibromo*-9-*aminomethylenefluorene* (VII), m.p. 212° (Dennis bar), undergoes brominolysis to 2 : 7 : 9-*tribromofluorene*-9-*aldehyde* (VIII), m.p. 236—237° (corr.; decomp.), also obtained from the 2 : 7-Br_2-aldehyde. (VII) is converted by glacial AcOH at 100° or, readily, by dil. H_2SO_4 into *di*-2 : 7-*dibromo*-9-*fluorenylmethyleneamine*, m.p. >300°, converted by Br in $CHCl_3$ followed by hydrolysis into (VIII). 9-Acetylfluorene and NH_3 in dry Et_2O at 0° give 9-α-*aminoethylidenefluorene* or α-*methyl*-$\Delta^{9\alpha}$-*fluorenemethylamine* (IX), m.p. 124·5—126·5° (corr.; decomp.) after softening, which rapidly darkens and becomes oily in a desiccator at room temp. (IX) is hydrolysed by 4% H_2SO_4 at room temp. to a mixture of monomeric and dimeric acetylfluorene. The *Ac* derivative of (IX) has m.p. 180·5—181·5° (corr.).

H. W.

Structure of aldehydo-acids and their tautomeric transformations. M. M. Schemjakin (*J. Gen. Chem. Russ.*, 1943, **13**, 290—300).—The properties of aldehydo-acids (*A*) and their reactions are reviewed from the point of view of ionotropy. The conditions under which one or other tautomeric form of (*A*) reacts and the influence of structural and external factors are described. Evidence is adduced to support the view that isolated, cryst. (*A*) are OH-lactones. The following compounds were tested with freshly prepared fuchsin–SO_2 reagent: *o*-CHO·C_6H_4·CO_2H showed coloration in 5—10 sec. and max. intensity in 1—2 min.; opianic acid showed coloration in 5—10 sec. and max. in 2—3 min.; CHO·CBr:CBr·CO_2H showed coloration in ½—1 min. on undissolved solid but only after ½ hr. in solution and the intensity increased very slowly; CHO·CPh:CH·CO_2H showed coloration in 2—3 min. on undissolved solid and intensity again increased very slowly; nitro-opianic acid (I) showed no coloration in 24 hr. In MeOH solution, bromo-opianic acid forms the OH-lactone Me ether (ψ-Me ester) (low yield) at room temp. in 1½ months or at the b.p. in 4—5 hr.; CHO·CBr:CBr·CO_2H similarly forms the ψ-ester at room temp. in 1 month. (I) with excess of piperidine for 5 min. (water-bath), dilution with EtOH, and cooling to 0° for 1—2 hr. gives its *dipiperidide*, m.p. 160—161° (60—70%, including the less pure product recovered from the mother-liquor by evaporation at room temp.).

R. C. P.

Polyenes. I. Synthesis and absorption spectra of the ionylideneacetones and related compounds. W. G. Young, L. J. Andrews, and S. J. Cristol (*J. Amer. Chem. Soc.*, 1944, **66**, 520—524).—Absorption spectra in 95% EtOH (max. in brackets below) indicate that α- (I) and β-ionone (II) yield polyenes without isomerisation. (I) [227 (ε 12,850) and 296 mμ. (ε 1950)] and (II) [296 (ε 8600) and 222 mμ. (ε 7640)] with Zn–CH_2Br·CO_2Et give OH-esters, which distil unchanged (β-ester, b.p. 153·5—155·5°/2—3 mm.) (cf. Karrer *et al.*, A., 1932, 852) but with $KHSO_4$ at 150° give Et α-, b.p. 162·5°/5—7 mm. [272 (ε 14,700) and 236 mμ. (ε 11,800)], and β-ionylideneacetate, b.p. 162·3—164·5°/6 mm. [283 mμ. (ε 18,950)], hydrolysed by KOH–EtOH to the derived α- [267 mμ. (ε 17,650)] and β-acids (III), liquid [294 (ε 13,700) and 260 mμ. (ε 12,900)] and cryst. (m.p. 124°) form [283 mμ. (ε 17,700)] (cf. *loc. cit.*). With PCl_3 and then $CdMe_2$–Et_2O these give α- (IV), b.p. 135·5—138°/2·5 mm. [285 mμ. (ε 14,500)], and β-ionylideneacetone (V) [ζ-2 : 6 : 6-trimethyl-Δ^2- and -Δ^1-*cyclo*hexenyl-δ-methyl-$\Delta^{\gamma\epsilon}$-hexadien-β-one, respectively], b.p. 131—132°/2·5 mm. [285 mμ. (ε 11,600)]. Slowly distilling (I) and (II) with CN·CH_2·CO_2Me and a little NH_2Ac and NH_4OAc in AcOH gives *Me* α-*cyano*-δ-2 : 6 : 6-*trimethyl*-Δ^2-, b.p. 154·5—157·5°/1·5 mm. [292·5 mμ. (ε 16,100)], and -Δ^1-*cyclo*hexenyl-β-methyl-Δ^α-pentenoate, b.p. 165—168°/2 mm. [353 (ε 12,000) and 286 mμ. (ε 10,300)], respectively, hydrolysed to the derived α-, an oil [286 mμ. (ε 14,300)], and β-acid, m.p. 160—163° (decomp.) (lit. an oil) [332 (ε 12,500) and 275 mμ. (ε 8700)], respectively. Decarboxylation then yields δ-2 : 6 : 6-*trimethyl*-Δ^2-, b.p. 147·5—150°/3 mm. [262·5 mμ. (ε 18,900)], and -Δ^1-cyclo*hexenyl*-β-*methyl*-$\Delta^{\alpha\gamma}$-*pentadienonitrile*, b.p. 138—140°/3 mm. [300 (ε 12,500) and 256 mμ. (ε 14,500)] [hydrolysed to (III), m.p. 122—125°, by KOH–EtOH], also obtained from (I) and (II), respectively, by CN·CH_2·CO_2H. With MgMeI–Et_2O or LiMe, these give (IV) and (V), respectively. (IV) gives a *semicarbazone*, m.p. 162·5—164°, but (V) gives an oil with NH·CO·NH_2·NH_2 or NH_2OH, although it reacts with Girard's reagent *T*. The structures of (IV) and (V) are proved by ozonolysis to *iso*geronic and geronic acid, respectively. In presence of PtO_2 in EtOH, (IV) and (V) absorb 3 H_2. NaOCl converts (I) and (II) into α-, an oil [<212·5 mμ. (ε >10,100)], and β-cyclo*citrylideneacetic acid*, m.p. 106—108° [277 mμ. (ε 9240)] (absorbs 1·96 H_2). (V) similarly gives (III), m.p. 122—124°.

R. S. C.

Pinacols and pinacolone from *p*-methoxyacetophenone. C. C. Price and G. P. Mueller (*J. Amer. Chem. Soc.*, 1944, **66**, 634—636).—Electrolytic reduction of *p*-OMe·C_6H_4·COMe (I) in KOAc–EtOH–H_2O (in absence or presence of EtOAc) gives βγ-*dihydroxy*-βγ-*di*-*p*-*anisyl*-n-*butane* (90%), *forms*, m.p. (II) 122—123° and (III) 168—169°. (III) is also obtained by Al–Hg in moist Et_2O. $Pb(OAc)_4$–AcOH rapidly oxidises (II) to (I). A drop of H_2SO_4 in Ac_2O rearranges (II) or (III) to αα-*di*-*p*-*anisylethyl Me ketone* (IV) (63%), m.p. 69·7—71·5°, cleaved by KOH at 170—180° to (*p*-OMe·C_6H_4)$_2$CHMe, m.p. 70—72° (lit. 59·4°). The structure of (IV) is proved by conversion of its *oxime*, m.p. 192—194° (insol. in alkali), by PCl_5–Et_2O into (*p*-OMe·C_6H_4)$_2$C:CH_2, m.p. 141—143°.

R. S. C.

Lignin and related compounds. LXXIX. Synthesis and properties of γ-hydroxy-α-3 : 4-dimethoxyphenylpropan-β-one. H. E. Fisher, M. Kulka, and H. Hibbert. **LXXX. Ethanolysis of α-acetoxy-α-4-acetoxy-3-methoxyphenylpropan-β-one and its relation to lignin structure.** L. Mitchell and H. Hibbert. **LXXXI. Properties of α-bromo-α-4-acetoxy-3-methoxyphenylpropan-β-one and relation to lignin structure.** L. Mitchell, T. H. Evans, and H. Hibbert. **LXXXII. Synthesis and properties of αγ-diacetoxy-α-4-acetoxy-3-methoxyphenylpropan-β-one and γ-chloro-α-acetoxy-α-4-acetoxy-3-methoxyphenylpropan-β-one and their relation to lignin structure.** J. A. F. Gardner and H. Hibbert (*J. Amer. Chem. Soc.*, 1944, **66**, 598—601, 602—604, 604—607, 607—610; cf. A., 1944, II, 176).—LXXIX. The properties of γ-3 : 4-*dimethoxyphenylpropan*-α-*ol*-β-*one* (I) (which is synthesised) confirm the authors' views on lignin components. 3 : 4 : 1-$(OMe)_2C_6H_3$·CO_2H (prep. from the aldehyde by aq. $KMnO_4$ in 90% yield) gives ($SOCl_2$) the chloride, m.p. 70—71°, and thence (CH_2N_2) the CHN_2 ketone, m.p. 76—77° (lit. 75°), converted by Ag_2O–MeOH–CO_2 at 55—60° into *Me homoveratrate* (72%), b.p. 110—113°/3 mm. The derived acid with $SOCl_2$ and then CH_2N_2–C_6H_6 yields a CHN_2 ketone, which added (in EtOH) to H_2O at 70° gives (I), b.p. 150—160° (bath)/0·05 mm. (*semicarbazone*, m.p. 123—124°; known acetate, m.p. 55—56°). Boiling 5% H_2SO_4 in 24 hr. or 72% H_2SO_4 at room temp. in 2 hr. gives 19·5 and 62·5%, respectively, of polymer from (I). (I) is very sensitive to alkali; in 1% aq. NaOH at 100° (24 hr.) it gives 54% and in 3% aq. NaOH at room temp. gives 80%, but in 3% NaOH–EtOH–H_2O (1 : 1) gives only 17% of polymer. It is unchanged (75% recovered) by boiling 5% aq. KOAc–CO_2 (12 hr.), but in 2% HCl–EtOH–CO_2 (48 hr.) gives 3 : 4 : 1-$(OMe)_2C_6H_3$·CO·CHMe·OEt (28%) and -$(OMe)_2C_6H_2$·CH(OEt)·COMe (52%).

LXXX. Ethanolysis of α-*acetoxy*-α-4-*acetoxy*-3-*methoxyphenylpropan*-β-*one* (II) supports the authors' views on lignin structure. (II) is obtained (80%) from 3 : 4 : 1-OMe·C_6H_2(OAc)·CHBr·COMe by AgOAc in 1 : 1 aq. dioxan at room temp. and has m.p. 97—98°. Ethanolysis first removes the labile Ac and then causes rearrangement. Thus, 2% HCl–EtOH–CO_2 at the b.p. (48 hr.) gives 3 : 4 : 1-OMe·C_6H_3(OH)·CO·CHMe·OEt (54·6%), -OMe·C_6H_3(OH)·CH(OEt)·COMe (16·7%), -OMe·C_6H_3(OH)·CO·COMe (7·3%), and -OMe·C_6H_3(OH)·CH_2·COMe (1·3%), and polymers (10%).

LXXXI. Further evidence is provided by the properties of α-*bromo*-α-4-*acetoxy*-3-*methoxyphenylpropan*-β-*one* (III). 4-*Acetoxy*-3-*methoxyphenylacetone* (prep. from the 4-OH-compound by Ac_2O–10% aq. NaOH at 0—10°), m.p. 47—48° (*semicarbazone*, m.p. 168—169°), with Br and a little Bz_2O_2 in $CHCl_3$ at <10° gives (III) (73%), m.p. 100—101° (*semicarbazone*, m.p. 180—181°), which with Ag_2SO_4 in 1 : 2 aq. dioxan–N_2 at room temp. gives 100% of AgBr, 35% of a polymer [? of 3 : 4 : 1-OMe·C_6H_2(OAc)·CH(OH)·COMe], and 60% of a mixture, whence removal of diketone as Ni glyoxime

salt and subsequent hydrolysis yields 3 : 4 : 1-$OMeC_6H_3(OH)\cdot CO\cdot COMe$ (**IV**) (44%) and -$OMe\cdot C_6H_3(OH)\cdot CH_2\cdot COMe$ (**V**) (27%). (**IV**) and (**V**) are probably formed by way of $(CHArAc)_2CO$ and, possibly, O<CHAr·CMe(OH)>O<CAr=CMe>O 3·4·1-$OMe\cdot C_6H_3(OH)\cdot CO\cdot CHMe\cdot OH$ and a little (**IV**) are also obtained from (**II**) by boiling $BaCO_3$–H_2O–N_2, and from (**III**) by boiling 5% aq. KOAc.

LXXXII. Reactions described below indicate that compounds, $OH\cdot CHAr\cdot CO\cdot CH_2\cdot OH \rightleftharpoons COAr\cdot CH(OH)\cdot CH_2\cdot OH$, may perhaps form building units of lignin to a limited extent. Treatment of 3 : 4 : 1-$OMe\cdot C_6H_3(OH)\cdot CH(OH)\cdot CN$ with HCl–EtOH at −10° and subsequent hydrolysis gives the Et ester (24%), m.p. 77°, and thence (2% NaOH; N_2) *4-hydroxy-3-methoxymandelic acid*, m.p. 133°, the *diacetate*, $+H_2O$, m.p. 142°, of which with $SOCl_2$ in boiling C_6H_6 (105 min.; not longer) gives the *diacetate acid chloride*, m.p. 72°, and thence *α-acetoxy-γ-diazo-α-4-acetoxy-3-methoxyphenylpropan-β-one* (88%), m.p. 129—130°. This does not react with cold AcOH but with AcOH–Ac_2O–N_2 at the b.p. gives *αγ-diacetoxy-α-4-acetoxy-3-methoxyphenylpropan-β-one* (**VI**) (77%), b.p. 65—70°/0·025 mm., and with HCl–Et_2O–C_6H_6 at 0° gives *γ-chloro-α-acetoxy-α-4-acetoxy-3-methoxyphenylpropan-β-one* (**VII**) (81%), m.p. 110—111°. In boiling NaOAc–AcOH–CO_2, (**VII**) gives 75% of Ni glyoxime salt and thence by 12N-H_2SO_4 at room temp. (**IV**). With boiling 2% HCl–EtOH–CO_2, (**VI**) gives 66% of polymer and 8% of (**IV**), with boiling 2% H_2SO_4 gives 8·6% of (**IV**), and with 72% H_2SO_4 gives 68% of polymer. R. S. C.

Synthesis of α-mesitylpropiomesitylene. R. C. Fuson, N. Rabjohn, W. J. Shenk, jun., and W. E. Wallace [with in part, Q. F. Soper, C. H. McKeever, S. Melamed, and J. L. Marsh] (*J. Org. Chem.*, 1944, **9**, 187—192).—A synthesis from mesitylacetonitrile (**I**) with other unsuccessful attempts is recorded. *Et mesitylacetate*, b.p. 152—153°/22 mm., is obtained from the acid chloride and EtOH, from the acid and EtOH containing p-$C_6H_4Me\cdot SO_3H$, and, with a *substance*, $C_{22}H_{26}ON$, m.p. 236—237°, from (**I**) and boiling H_2SO_4–EtOH. It could not be caused to react with CH_2O or EtOAc but with $Et_2C_2O_4$ it yields a compound regarded as *Et₂ mesitylmalonate*, m.p. 49—80°, which could not be methylated. (**I**) fails to condense with CH_2O but is readily transformed by EtOAc in EtOH–NaOEt into *α-mesitylacetoacetonitrile*, m.p. 117—118°, converted by MeI and NaOH in EtOH into the *O-Me* derivative, b.p. 152—156°/3—4 mm. This is hydrolysed by boiling AcOH–H_2SO_4 to *mesitylacetone*, m.p. 60—61°, also obtained (impure) from *s*-$C_6H_3Me_3$, $COMe\cdot CH_2Cl$, and $AlCl_3$ or from (**I**) and a large excess of MgMeI. HCO_2Et, (**I**), and NaOEt in boiling EtOH afford *β-hydroxy-α-mesitylacrylonitrile*, m.p. 131·5—132·5° or 126·5—127·5° after several hr. (*benzoate*, m.p. 127—128°, unaffected by H_2 in presence of PtO_2), converted by NH_2Ph in boiling EtOH into *β-anilino-α-mesitylacrylonitrile*, m.p. 151·5—153°. MeCHO and Mg mesityl bromide give (?) *di(mesitylmethylcarbinyl) ether*, m.p. 94—95°; treatment of the crude condensation product with HCl in dry Et_2O followed by Mg and then 2 : 4 : 6 : 1-$C_6H_2Me_3\cdot COCl$ lead to mesitoic acid and (?) *βγ-dimesitylbutane*, m.p. 139—140°. *s*-$C_6H_3Me_3$, $CHMeCl\cdot COCl$, and $AlCl_3$ in CS_2 at 5° yield unstable *α-chloropropiomesitylene*, b.p. 99—100°/1·5 mm. [3 : 5-$(NO_2)_2$-derivative, m.p. 127·5—128·5°]; *β-chloro-3 : 5-dinitropropiomesitylene* has m.p. 190—191·5°. Addition of (**I**) to $NaNH_2$ in Et_2O leads to α-mesitylpropionitrile, b.p. 160—165°/35 mm., hydrolysed by boiling glacial AcOH–conc. H_2SO_4 to α-mesitylpropionic acid, m.p. 102—103° (*amide*, m.p. 100—101°). This with $SOCl_2$ followed by *s*-$C_6H_3Me_3$ and $AlCl_3$ gives α-mesitylpropiomesitylene, b.p. 160—165°/1—2 mm. m.p. 74—75°. (**I**), $NaNH_2$, and CH_2PhCl yield *β-phenyl-α-mesitylpropionitrile*, b.p. 173—180°/2—5 mm., hydrolysed by boiling H_2SO_4–AcOH to the *acid*, m.p. 136—137°, with some *amide*, m.p. 119—120°. H. W.

Rearrangement of arylamides of aromatic and aliphatic acids under the action of aluminium chloride. D. N. Kursanov (*J. Gen. Chem. Russ.*, 1943, **13**, 286—289).—NHPhAc and NHPhBz with $AlCl_3$ at 200° for 1 hr. and 5 hr. respectivelv, give tarry products containing p-$NH_2\cdot C_6H_4\cdot COR$ [R = Me (12%), R = Ph (5%)]. NHPhAc and $AlCl_3$, in presence of PhMe at 200° in a sealed tube for 2 hr., yield 16·2% of p-$C_6H_4Me\cdot COMe$, indicating that the rearrangement proceeds through preliminary cleavage of the acyl group. R. C. P.

Volatile vegetable substances. XXIX. Isolation of a tricyclic isomeride of ionone. Y. R. Naves and P. Bachmann (*Helv. Chim. Acta*, 1944, **27**, 645—649).—Treatment of the portion of the products of cyclisation of ψ-ionone which does not react with $NaHSO_3$ with Girard's reagent *P* gives a mixture, b.p. 92—94°/4·6 mm., of ketones, which affords a *semicarbazone*, m.p. 209—209·5°, hydrolysed to *tricycloionone* (**I**), b.p. 90—90·5°/4 mm., the colour reactions of which are described. The tricyclic character of (**I**) is established by physical evidence. (**I**) gives a *δ-phenylsemicarbazone*, m.p. 186·5—187°, and a 2 : 4-*dinitrophenylhydrazone*, m.p. 151·1—152°. (**I**) is reduced by Na and boiling EtOH to *tricycloionol*, b.p. 98—99°/2·5 mm. (*acetate*, b.p. 95—96°/1·2 mm.), which is not hydrogenated (PtO_2 in AcOH at 60°). NaOI and (**I**) do not give CHI_3. H. W.

Three coloured isomeric forms of benzaurins and phthaleins. Structure of form *A*. P. Ramart-Lucas (*Compt. rend.*, 1943, **217**, 24—26).—The fuchsone structure for benzaurin is discussed (cf. A., 1939, II, 260, 321). A. T. P.

Nature of the isomerism of the three coloured forms of benzaurins and phthaleins. Possible metamorphosis of derivatives. P. Ramart-Lucas (*Compt. rend.*, 1943, **217**, 114—116; cf. A., 1939, II, 321).—Absorption spectra of benzaurin (**I**), its Me ether (**II**), p-$CPh_2\cdot C_6H_4\cdot O$, $(p\text{-}OMe\cdot C_6H_4)_2CPh\cdot OH$, $CPh_3\cdot OH$, and $CHPh_3$ are compared. (**II**), like (**I**), can exist in three forms, one of which (fuchsone, quinonoid form) exists in neutral, and one in acid, medium. A theory based on differing electronic states of the central C is suggested. A. T. P.

Synthesis of *p*-benzoquinone. J. H. Billman, B. Wolnak, and D. K. Barnes (*J. Amer. Chem. Soc.*, 1944, **66**, 652).—93—95% of p-$O\cdot C_6H_4\cdot O$ is obtained by adding NH_4VO_3 to quinol and $NaClO_3$ in 2% H_2SO_4 at 40—42° (30 min.) and then cooling. R. S. C.

Easy method for the preparation of dianthraquinone. Action of pyridine on dianthranol and dianthrone. A. Schonberg and A. F. A. Ismail (*J.C.S.*, 1944, 307).—Oxidation of dianthranol (**I**) with p-$O\cdot C_6H_4\cdot O$ in $COMe_2$ at room temp. gives dianthraquinone (approx. quant. yield) with quinhydrone. Dianthrone (**II**) or (**I**) with C_5H_5N affords a *compound*, $C_{38}H_{28}O_2N_2$, m.p. 190° (efferv.), remelts 229°, which with HCl–EtOH forms (**II**). F. R. S.

IV.—STEROLS AND STEROID SAPOGENINS.

Chromatography and mesomerism in the sterol series. Salkowski's reaction. P. Meunier (*Compt. rend.*, 1943, **217**, 78—80).—The red colour of cholesterol (**I**) in $CHCl_3$–H_2SO_4 is attributed to mesomerism. This is supported by the production of some $\Delta^{3:5}$-cholestadiene, m.p. 79° (absorption max. at 229, 235, and 245 mμ.) (cf. Schoenheimer *et al.*, A., 1936, 1105), in addition to dicholesteryl ether, from (**I**) (method : Bills *et al.*, A., 1926, 981). A. T. P.

Steroids and sex hormones. XCVII. Relationships between constitution and optical activity in the cholic acid series. P. A. Plattner and H. Heusser (*Helv. Chim. Acta*, 1944, **27**, 748—757).—The observation of Bernstein *et al.* (A., 1942, II, 177) that changes in the side-chain of the sterols have little influence on $[M]_D$ is confirmed; the effect is very small when such changes occur at a distance from the asymmetric $C_{(20)}$ and when a new centre of asymmetry is not developed. The behaviour of Me cholate on partial or complete acetylation shows that the contributions to $[M]$ of the asymmetric centres at $C_{(3)}$, $C_{(7)}$, and $C_{(12)}$ are largely independent of one another. Marked differences are found for the free, partly acetylated acids. It appears therefore that unpredictable influences also play a part. The relative independence of the asymmetric centres at $C_{(7)}$ and $C_{(12)}$ of the sterol skeleton is shown by observations of the effect of introducing OH groups into lithocholic acid. The following are described : *Me triacetylcholate*, m.p. 90·5—91°, $[\alpha]_D^{14}$ +81·8° in EtOH, $[\alpha]_D^{17}$ +76·8° in $CHCl_3$; *Me triformylcholate*, m.p. 133·5—134·5°, $[\alpha]_D^{14}$ +90·0° in EtOH, $[\alpha]_D^{17}$ +86·0° in $CHCl_3$; 3(α)-hydroxy-7(α) : 12(β)-diacetoxycholanic acid, m.p. 202—203°, $[\alpha]_D^{14}$ +71·6° in EtOH (*Me* ester, m.p. 57—59°, $[\alpha]_D^{14}$ +72·0° in EtOH, +63·7° in $CHCl_3$); 12(β)-hydroxy-3(α) : 7(α)-diacetoxycholanic acid, m.p. 261—263°, $[\alpha]_D^{17}$ +49·8° in EtOH (*Me* ester, m.p. 182—183°, $[\alpha]_D^{14}$ +35·3° in EtOH, +31·0° in $CHCl_3$); Me 7(α) : 12(β)-dihydroxy-3(α)-acetoxycholanate, m.p. 149·5—150°, $[\alpha]_D^{14}$ +52·8° in EtOH, $[\alpha]_D^{15}$ +47·6° in $CHCl_3$; 12-keto-3(α) : 7(α)-diacetoxycholanic acid, m.p. 229—230°, $[\alpha]^{17}$ +86·5° in $CHCl_3$ (*Me* ester, m.p. 177—178·5°, $[\alpha]_D^{17}$ +83·5° in $CHCl_3$); chenodeoxycholic [3(α) : 7(α)-dihydroxycholanic] acid, m.p. 140—141·5°, $[\alpha]^{17}$ +12·5° in $CHCl_3$ (*Ba* salt); 3(α) : 7(α)-diformoxycholanic acid, m.p. 132·5—133·5° and 180—182°, $[\alpha]_D^{16}$ +31·0° in EtOH. H. W.

Bile acids and related substances. XXIX. Derivative of bisnordeoxycholic acid and of 3(α) : 11(α)-dihydroxybisnorcholanic acid. A. Lardon and T. Reichstein (*Helv. Chim. Acta*, 1944, **27**, 713—726).—Me 3(α) : 12(β)-dihydroxybisnorcholanate (Me bisnordeoxycholate) (**I**) is cautiously oxidised by CrO_3 in AcOH to *Me* 3 : 12-*diketobisnorcholanate*, m.p. 139—141°, $[\alpha]_D^{15}$ +82·1°±2° in $COMe_2$. Partial acetylation of (**I**) by Ac_2O in boiling C_6H_6 affords *Me* 12(β)-*hydroxy*-3(α)-*acetoxybisnorcholanate*, m.p. 198—199°, $[\alpha]_D^{18}$ +54·7°±1·5° in $COMe_2$, oxidised (CrO_3 in AcOH) to the 12-*keto*-ester, m.p. 168—170°, $[\alpha]_D^{20}$ +93·9°±1·5° in $COMe_2$. Energetic acetylation (Ac_2O–C_5H_5N at 100°) of (**I**) yields *Me* 3(α) : 12(β)-*diacetoxybisnorcholanate*, m.p. 169—170°, $[\alpha]_D^{13}$ +84·4°±1° in $COMe_2$, partly hydrolysed (1% HCl–MeOH at 16°) to *Me* 3(α)-*hydroxy*-12(β)-*acetoxybisnorcholanate*, m.p. 137—138°, $[\alpha]_D^{20}$ +73·2°±1° in $COMe_2$, oxidised to the 3-*keto*-ester (**II**), m.p. 136—137°, $[\alpha]_D$ +64·8°±1·5° in $COMe_2$, and an unidentified *by-product*, $C_{33}H_{38}O_5$, m.p. 164—165°, $[\alpha]_D^{15}$ +73·4°±1·5° in $COMe_2$. Alkaline hydrolysis and esterification (CH_2N_2) of (**II**), particularly if the conditions are not too drastic, leads mainly to *Me* 12(β)-*hydroxy*-3-*ketobisnorcholanate*, m.p. 204—206°, $[\alpha]_D^{13}$ +38·6°±1·5° in $COMe_2$, with some

Me 12(β)-hydroxy-3-ketobisnor-20-*iso*cholanate [only obtained amorphous but identified by conversion into the acetate, m.p. 169—171°, and oxidation to the 3 : 12-$(CO)_2$-compound, double m.p. 116—118° and 140—141°], and by-products, m.p. 142—144° (oxidised to a *compound*, $C_{23}H_{34}O_4$, m.p. 181—183° and m.p. 177—179° (similarly oxidised to a *substance*, $C_{23}H_{34}O_4$, m.p. 164—166°). *Me* 3-*keto*-12(β)-*benzoyloxy*-, m.p. 135—136°, $[\alpha]_D^{13}$ +46·8°±1·5° in $COMe_2$, and *Me* 3(α) : 12(β)-*dibenzoyloxy*-, m.p. 170—171°, -*bisnorcholanate* are described. (**I**) is converted by anthraquinone-2-carboxyl chloride in abs. C_5H_5N–PhMe at 100° into *Me* 3(α) : 12(β)-*dianthraquinone*-2′-*carboxybisnorcholanate*, m.p. 221—223° [accompanied under less drastic conditions by the 12(β)-*hydroxy*-3(α)-*anthraquinone*-2′-*carboxy* ester, m.p. 271—273°], hydrolysed by KOPh in boiling EtOH–dioxan to the 3(α)-hydroxy-12(β)-anthraquinone-2′-carboxy ester [*acetate* (*A*), m.p. 116—118°, becomes opaque at ~100°]. Thermal fission of the above monobenzoate or of Me 3-keto-12(β)-anthraquinone-2′-carboxybisnorcholanate, a resin, leads to *Me* 3-*keto*-Δ^{11}-*bisnorcholenate* (**III**), m.p. 122—123°, $[\alpha]_D^{13}$ +20·0°±1·5° in $COMe_2$, reduced (H_2, Raney Ni in MeOH containing NaOH) and then acetylated to Me 3(α)- (**IV**), m.p. 101—102°, new $[\alpha]_D^{15}$ +32·2°±1° in $COMe_2$ [also obtained by thermal fission of (*A*)], and *Me* 3(β)-*acetoxy*-Δ^{11}-*bisnorcholenate*, m.p. 139—140°, $[\alpha]_D^{13}$ +13·8°±1° in $COMe_2$. (**III**) and NHAcBr in aq. $COMe_2$ at 16° followed by CrO_3–aq. AcOH afford Me 12-bromo-3 : 11-diketobisnorcholanate (**V**), m.p. 198—202°, converted by Zn dust and NaOAc in AcOH at 100° into *Me* 3 : 11-*diketobisnorcholanate* (**VI**), m.p. 199—201°, $[\alpha]_D$ +47·6°±1·5° in $COMe_2$; *Me* 3 : 12-*diketo*-Δ^9-*bisnorcholenate*, m.p. 136—138°, $[\alpha]_D^{16}$ +73·1°±1·5° in $COMe_2$, and (**III**) are obtained similarly from the by-products of (**V**). (**VI**) is hydrogenated (PtO_2 in AcOH) with subsequent acetylation (Ac_2O in C_5H_5N at 60°) and re-oxidation (CrO_3 in AcOH at room temp.) to *Me* 11-*keto*-3(α)-, m.p. 148—150° (from MeOH) or 142—144° and then 153—154° (from Et_2O–light petroleum), $[\alpha]_D^{15}$ +57·6°±2° in $COMe_2$, and *Me* 11-*keto*-3(β)-*acetoxybisnorcholanate*, m.p. 163—165°, $[\alpha]_D^{13}$ +29·3°±1·5° in $COMe_2$; the former is also obtained from (**IV**). *Me* 11(α)-*hydroxy*-3(α)-*acetoxy*-, m.p. 137—139°, $[\alpha]_D^{15}$ +56·5°±1·5° in $COMe_2$, 3(α) : 11(α)-dihydroxy-, m.p. 75—85° (? hydrate), $[\alpha]_D^{16}$ +38·8°±1° in $COMe_2$, 11(α)-*hydroxy*-3(β)-*acetoxy*-, m.p. 173—175°, $[\alpha]_D^{12}$ +33·7°±1·5° in $COMe_2$, and 3(β) : 11(α)-dihydroxy-, m.p. 139—140°. $[\alpha]_D^{16}$ +34·2°±0·8° in $COMe_2$, -bisnorcholanate are described. M.p. are corr. (block); limits of error ±2°. H. W.

Degradation of bile acid derivatives. R. P. Jacobsen (*J. Amer. Chem. Soc.*, 1944, **66**, 662).—Bile acids are degraded in good yield by the following reactions. $CHRMe{\cdot}[CH_2]_2{\cdot}COCl$ [+$CdPh_2$] → $CHRMe{\cdot}[CH_2]_2{\cdot}COPh$ → mixed $CHRMe{\cdot}CH_2{\cdot}CHBr{\cdot}COPh$ → $CHRMe{\cdot}CH_2{\cdot}CH(OAc){\cdot}COPh$ $CHRMe{\cdot}CH_2{\cdot}CH(OH){\cdot}COPh$ → ($CuSO_4$–aq. C_5H_5N) $CHRMe{\cdot}CH_2{\cdot}CO{\cdot}COPh$ (65—70%) → $CHRMe{\cdot}CH{:}C(OAc){\cdot}COPh$ → $CHRMe{\cdot}CO_2H$. The following are described: *cholophenone* [*Ph norcholyl ketone*], +0·5H_2O, m.p. 174—176·5°, $[\alpha]_D^{20}$ +26° [*triacetate*, m.p. 120·3—121°, $[\alpha]_D^{20}$ +79°; 2 : 4-*dinitrophenylhydrazone*, m.p. 221—222·5°; *oxime*, m.p. 214—217° (decomp.)]; 23(? β)-*bromocholophenone triacetate*, +H_2O, m.p. 108·5—111·5°, $[\alpha]_D^{20}$ +95°; 23(? α)-*acetoxycholophenone triacetate*, +0·5H_2O, m.p. 180—182°, $[\alpha]_D^{20}$ −10°; *Ph bisnorcholyl diketone triacetate*, m.p. 166—169° (after drying, 161·5—166°), $[\alpha]_D^{20}$ +92° (the 7 : 12-*diacetate* has m.p. 201—203·5°, $[\alpha]_D^{20}$ +80°); 3-*phenyl*-2-*bisnorcholyl*-*quinoxaline triacetate*, m.p. 217—218·5°. [α] are in $CHCl_3$.

R. S. C.

Adsorption of œstrone, œstriol, and α-œstradiol on a chromatographic column. B. F. Stimmel (*J. Biol. Chem.*, 1944, **153**, 327—333).—Strongly phenolic may be separated from weakly phenolic œstrogens by means of a liquid chromatogram using activated Al_2O_3, the weakly phenolic being eluted by a 9 : 1 C_6H_6–MeOH mixture and the strongly phenolic by a 4 : 1 mixture. The Al_2O_3 is inactivated by the process and its subsequent use is inadvisable.

H. G. R.

Synthesis of compounds related to sex hormones. W. E. Bachmann and R. D. Morin (*J. Amer. Chem. Soc.*, 1944, **66**, 553—557).—9 : 6 : 7 : 8-Tetrahydro-1-naphthylamine (prep. from α-$C_{10}H_7{\cdot}NH_2$ by Na and fusel oil in 84% yield) gives (diazo-reaction) the 1-I-derivative (66%), b.p. 153—158°/20 mm., and thence, successively, [Grignard; $(CH_2)_2O$] β-5 : 6 : 7 : 8-tetrahydro-1-naphthylethyl alcohol (57%), b.p. 125—135°/0·4 mm., (PBr_3) the derived bromide (62%), b.p. 113—118°/0·05 mm., [$CHNa(CO_2Et)_2$; then hydrolysis and heating at 180°] γ-5 : 6 : 7 : 8-tetrahydronaphthyl-1-butyric acid (65%), m.p. 94—95°, and (acid chloride; $SnCl_4$) 1-keto-*s*-octahydrophenanthrene (**I**) (88%), m.p. 80·5—82°. $Me_2C_2O_4$ and (**I**) give *Me* 1-*keto*-s-*octahydrophenanthrene*-2-*glyoxylate* (89%), m.p. 103—104°, converted by heating with powdered, soft glass at 180° into *Me* 1-*keto*-s-*octahydrophenanthrene*-2-*carboxylate* (88%), m.p. 83—85°, which with NaOMe and MeI in MeOH–C_6H_6 gives *Me* 1-*keto*-2-*methyl*-s-*octahydrophenanthrene*-2-*carboxylate*, m.p. 77—78° (derived *acid*, m.p. 87—88°). The Reformatsky reaction then gives *Me* 1-*hydroxy*-2-*carbomethoxy*-2-*methyl*-s-*octahydro*-1-*phenanthrylacetate* (76—81%), m.p. 102—103° [converted by hot KOH–MeOH–H_2O into the 2-Me derivative of (**I**)], which with $SOCl_2$–C_5H_5N and then KOH–EtOH–H_2O gives 2-*carboxy*-2-*methyl*-s-*octahydro*-1-*phenanthrylideneacetic acid* (92%), m.p. 140—141° (gas). This or an unpurified solution of it with 2% Na–Hg in aq. KOH gives 2-*carboxy*-2-*methyl*-s-*octahydro*-1-*phenanthrylacetic acid*, α- (40—43%), m.p. 218—219°, and β-*form* (46—50%), m.p. 162—163°, the Me_2 esters (prep. by CH_2N_2), α-, m.p. 70·5—71°, and β-*form*, m.p. 81·5—82·5°, of which with hot NaOH–MeOH–H_2O give 2-*carbomethoxy*-2-*methyl*-s-*octahydro*-1-*phenanthrylacetic acid* (95—98%), α-, m.p. 121—122°, and β-*form*, m.p. 141—142°. Arndt–Eistert reactions then yield *Me* β-2-*carbomethoxy*-2-*methyl*-s-*octahydro*-1-*phenanthrylpropionate*, α- (75%), m.p. 63·5—64·5°, and β-form, an oil, cyclised by NaOMe in boiling C_6H_6 to *Me* 1 : 2 : 3 : 4-*tetrahydro*-17-*equilenone*-16-*carboxylate*, α- (90%), m.p. 124—125° (dark green $FeCl_3$ colour), and β-*form* (85%), m.p. 121—122° (greenish-brown $FeCl_3$ colour), which in boiling HCl–AcOH–H_2O–N_2 give 1 : 2 : 3 : 4-*tetrahydro*-17-*equilenone*, α- (88%), m.p. 72—73° (*semicarbazone*, m.p. 243—244°), and β-*form* (79%), m.p. 114—115° (vac.) [*semicarbazone*, m.p. 274—275° (vac.)] (cf. Marker *et al.*, A., 1940, II, 95), converted by S at 210° into the α- and β-forms, respectively, of 17-equilenone.

2-$C_{10}H_7{\cdot}OMe$ and $(CH_2{\cdot}CO)_2O$ give 6 : 2-$OMe{\cdot}C_{10}H_6{\cdot}CO{\cdot}[CH_2]_2{\cdot}CO_2H$, m.p. 147—148°, the Et ester, m.p. 107·5—108°, of which affords (Reformatsky) the *lactone* (**II**) (84%), m.p. 121—122°, of α-Me α′-H β-hydroxy-β-6-methoxy-2-naphthyladipate. Hot N-aq. NaOH–MeOH converts (**II**) into β-6-*methoxy*-2-*naphthyl*-Δ^{α}-*butene*-αδ-*dicarboxylic acid* (**III**) (98%), m.p. 194—195°, the Me_2 ester, b.p. 190°/0·05 mm., of which yields by cyclisation 3-6′-*methoxy*- (80%), m.p. 125—126°, and thence (boiling HCl–AcOH–H_2O–N_2) 3-6′-*hydroxy*-2′-*naphthyl*-Δ^2-cyclo*pentenone* (**IV**), m.p. 252—253° (vac.) {*Me ether*, m.p. 169—170° [*semicarbazone*, m.p. 250—251° (vac.), reduced by NaOMe–EtOH at 180° to the known 1-6′-methoxy-2′-naphthylcyclopentene, m.p. 141—142°]; *semicarbazone*, m.p. 260—262° (vac.)}. 2% Na–Hg in aq. KOH reduces (**III**) to β-6-*methoxy*-2-*naphthyladipic acid*, m.p. 164—165°, the Me_2 ester, b.p. 180—190°/0·05 mm., of which by successive cyclisation, hydrolysis, decarboxylation, and demethylation affords 3-6′-*hydroxy*-2′-*naphthyl*cyclo*pentanone* (83%), m.p. 176—176·5° (*semicarbazone*, m.p. 212—213°), also obtained from (**IV**) by H_2–Pd–C in AcOH. By similar reactions β-$C_{10}H_7{\cdot}CO{\cdot}[CH_2]_2{\cdot}CO_2H$ gives the *lactone*, m.p. 111—112°, of α-Me α′-H β-hydroxy-β-2-naphthyladipate, β-2-*naphthyl*-Δ^{α}-*butene*-αδ-*dicarboxylic acid*, m.p. 179—180° (Me_2 ester, b.p. 170—180°/0·05 mm), 3-2′-naphthyl-Δ^2-cyclo*pentenone* (**V**), m.p. 126—127° [semicarbazone, m.p. 240—241° (lit. 244°)], 1-2′-naphthylcyclopentene, β-2-*naphthyladipic acid*, m.p. 153—154°, and 3-2′-naphthylcyclopentanone, m.p. 65—66° (lit. 61°) [semicarbazone, m.p. 199—199·5° (lit. 196—197°)]. 2-Chloroacetyl-5 : 6 : 7 : 8-tetrahydronaphthalene yields by similar reactions γ-keto-γ-5 : 6 : 7 : 8-tetrahydro-2-naphthylbutyric acid, β-5 : 6 : 7 : 8-*tetrahydro*-2-*naphthyl*-Δ^{α}-*butene*-αδ-*dicarboxylic acid*, m.p. 185—186°, 3-5′ : 6′ : 7′ : 8′-*tetrahydro*-2′-*naphthyl*-Δ^2-cyclo*pentenone*, m.p. 82—82·5° [*semicarbazone*, m.p. 235—236°; and thence by Pd–C–N_2 at 320° (**V**)], β-5 : 6 : 7 : 8-*tetrahydro*-2-*naphthyladipic acid*, m.p. 159·5—160°, and 3-5′ : 6′ : 7′ : 8′-*tetrahydro*-2′-*naphthyl*cyclo*pentanone*, m.p. 73—74° (*semicarbazone*, m.p. 207—208°). R. S. C.

Steroids and sex hormones. XCVI. Rearrangement products of 2-acetoxycholestan-3-one. L. Ruzicka, P. A. Plattner and M. Furrer (*Helv. Chim. Acta*, 1944, **27**, 727—737).—2-Acetoxy- (**I**) and 2-hydroxy-cholestan-3-one (**II**) are shown to be very labile compounds. Catalytic hydrogenation (Pt) of (**I**) in neutral or acidic solution affords a mixture (**III**) of compounds from which *cholestan*-1-*yl acetate*, m.p. 80—81°, $[\alpha]_D$ +9·5° in $CHCl_3$, is isolated in small amount. It is hydrolysed by boiling KOH–MeOH to *cholestan*-1-*ol* (**IV**), m.p. 165·5—166° $[\alpha]_D$ +14° in $CHCl_3$ (*benzoate*, m.p. 107—108°, $[\alpha]_D$ +0·2° in $CHCl_3$), oxidised (CrO_3 in AcOH) to *cholestan*-1-*one* (**V**), m.p. 120—120·5°, $[\alpha]_D$ +41° in $CHCl_3$, which is reduced (N_2H_4,H_2O and Na in $C_5H_{11}{\cdot}OH$ at 190°) to cholestane (**VI**). The constitution of (**V**) is based on its non-identity with any known cholestanone. The following also are isolated from (**III**): *acetoxycholestanol*-A, m.p. 168—169°, [α] +41° in $CHCl_3$ (*acetate*, m.p. 161—162°, $[\alpha]_D$ +33° in $CHCl_3$; *benzoate*, m.p. 180—182°; p-*toluenesulphonate*, m.p. 146·5—147·5°), oxidised (CrO_3) to *acetoxycholestanone*-A, m.p. 145—146°, $[\alpha]_D$ +1° in $CHCl_3$, which greatly depresses the m.p. of (**I**); *acetoxycholestanol*-B, m.p. 182·5—183·5°, and -C, m.p. 174—176°; (?) cholestane-2 : 3-diol, m.p. 196—197°, and a mixture of various diols. Reduction (Clemmensen) of (**I**) gives (**VI**) exclusively. The following are obtained by reduction (Wolff–Kishner) of (**I**): (**VI**) with smaller proportions of (**IV**), cholestan-4-ol, m.p. 189·5—190° (*acetate*, m.p. 112·5—113°, $[\alpha]_D$ +16° in $CHCl_3$; *benzoate*, m.p. 117·5—118°), oxidised to *cholestan*-4-*one*, m.p. 99—99·5°, $[\alpha]_D$ +29·5° in $CHCl_3$, a cholestan-2-ol (the presence of which is established by oxidation to cholestan-2-one), and two *azines*, $C_{54}H_{92}N_2$, m.p. 235—242° (decomp.) and 200—210° (decomp.). Hydrolysis of (**I**) in C_6H_6 with K_2CO_3 in aq. MeOH gives (**II**) in moderate yield with large amounts of a (?) 3-*hydroxycholestan*-4-*one* (**VII**), m.p. 173—175°, softens at 171°, $[\alpha]_D$ +14·5° in $CHCl_3$ [*acetate* (**VIII**], m.p. 143·5—144·5°, $[\alpha]_D$ −7·5° in $CHCl_3$], converted by HBr–AcOH–$CHCl_3$ at 100° into cholestan-4-one, m.p. 98—99°. The sole isolable product of the hydrolysis of (**I**) by KOH is a *OH-ketone* [? Δ^3-*cholestene*-3 : 4-*diol*], m.p. 125·5—127°, $[\alpha]_D$ +35° in $CHCl_3$, isomeric with (**VII**) and from which it is distinguished by its colour with $C(NO_2)_4$. It is converted by Ac_2O–C·C_5H_5N into (**VIII**). It and (**VII**) are converted by alkaline H_2O_2 into the dihydro-Diels' acid. Δ^3-3-

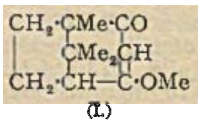
Acetoxycholesten-2-one is hydrogenated (Raney Ni in EtOH) to 3(β)-*acetoxycholestan-2-one* (**IX**), m.p. 145·5—146·5°, $[\alpha]_D$ +73° in $CHCl_3$ [*oxime* (**X**), m.p. 178—179·5° (decomp.)], reduced (Wolff–Kishner) to (**VI**). Alkaline hydrolysis (KOH–MeOH) of (**X**) yields 3(β)-*hydroxycholestan-2-oneoxime*, m.p. 207—208° (decomp.). NaOH–MeOH at 20° converts (**IX**) into 3(β)-*hydroxycholestan-2-one*, m.p. 104—105°, $[\alpha]_D$ +65° in $CHCl_3$, oxidised to the dicarboxylic acid, m.p. 193—195°, of Windaus *et al.* M.p. are corr. H. W.

Constituents of the adrenal cortex and related substances. LXVII. Attempted preparation of ætiocholane-3(α) : 12(β)-diol-17-one by systematic degradation. B. Koechlin and T. Reichstein (*Helv. Chim. Acta*, 1944, **27**, 549—566; cf. A., 1944, II, 106).—Five known methods and one new one have been applied to the degradation of derivatives of ætiocholanic acid or pregnan-20-one to derivatives of ætiocholan-17-one and particularly to the prep. of ætiocholane-3(α) : 12(β)-diol-17-one (**I**). This has been obtained only from pregnane-3(α) : 12(β)-diol-20-one by the method of Marker *et al.* (A., 1942, II, 230, 264) but the yield is unsatisfactory. Unsuccessful attempts to obtain cryst. diphenyl-3(α) : 12(β)-diacetoxyætiocholanylcarbinol or the corresponding methene from Me ætiodeoxycholate (cf. A., 1941, II, 140) are described; a cryst. *by-product*, $C_{30}H_{40}O_5$, m.p. 152—153°, has been isolated. Treatment of *allo*pregnane-3(β)-ol-20-one acetate with MgMeBr and subsequent acetylation affords 20-methyl*allo*pregnane-3(β) : 20-diol 3-monoacetate (**II**), needles which pass into hexagonal plates at 185—190°, m.p. 200—202°, in good yield (cf. Butenandt *et al.*, A., 1935, 1033). (**II**) loses H_2O in boiling AcOH, giving mainly 20-*methyl*-Δ^{20}-*allopregnene*-3(β)-*ol acetate* (**III**), m.p. 111—114°, $[\alpha]_D^{15}$ ±0°±2° in $COMe_2$, with smaller quantities of an *isomeride* (**IV**), m.p. 65—67°, $[\alpha]_D^{16}$ −57·2°±1·5° in $COMe_2$, and traces of 20-methyl-Δ^{17}-*allo*pregnen-3(β)-ol acetate, m.p. 144°. (**II**) sublimes unchanged at 145° (bath)/high vac., but is partly dehydrated by repeated distillation at 210°/12 mm., whereby the main product is (**III**). This is formed almost exclusively from (**II**) and $POCl_3$–C_5H_5N at 130°, and (**IV**) is almost the sole product of the action of P_2O_5 (in C_6H_6) or of HCO_2H on (**II**). The consitution of (**III**) is deduced from its ozonisation to *allo*pregnan-3(β)-ol-20-one acetate; it is hydrogenated to 20-*methyl*allo*pregnan*-3(β)-*ol acetate*, m.p. 124—125°. (**IV**) is hydrolysed to the corresponding alcohol, m.p. 144—145° after a transformation at ~140°. Ozonisation of (**IV**) gives some acidic products but mainly neutral material from which a *substance*, $C_{24}H_{38(40)}O_{4(5)}$, m.p. 186—188°, $[\alpha]_D^{17}$ +22·1°±3° in dioxan, is isolated which does not react with $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$. Attempted chromatographic purification of this material by Al_2O_3 leads to *compounds*, $C_{24}H_{38}O_4$, m.p. 156—161°, and 202—205°. (**IV**) is hydrogenated (PtO_2 in AcOH) to a *substance*, $C_{24}H_{40}O_2$, m.p. 81—84°, which does not give a yellow colour with $C(NO_2)_4$. Ag 3(β)-acetoxyætio*allo*cholanate is largely unattacked by Br in CCl_4 at room temp. and subsequently at incipient boiling. Addition of Br–AcOH to *allo*pregnan-3(β)-ol-20-one acetate in AcOH containing HBr and treatment of the product with KOH–MeOH gives neutral products which, after acetylation, afford *Me* 3(β)-*acetoxy*-17-*methyl*ætio*allocholanate*, m.p. 200—202°, which does not give a colour with $C(NO_2)_4$ and acidic products from which after methylation, acetylation, ozonolysis, and hydrolysis androstan-3(β)-ol-17-one, m.p. 175°, is obtained in ~7% yield. A similar series of changes starting from pregnane-3(α) : 12(β)-diol-20-one diacetate leads to *Me* 3(α) : 12(β)-*diacetoxy*-17-*methyl*ætio*allocholanate*, m.p. 163—165°, and the diacetate, m.p. 160—162°, $[\alpha]_D^{16}$ +186·3°±2° in $COMe_2$, of (**I**). Gradual addition of NaOEt–EtOH to a solution of *allo*pregnane-3(β)-ol-20-one acetate and PhCHO in abs. EtOH gives 21-benzylidene*allo*pregnan-3(β)-ol-20-one acetate, m.p. 211—214° (lit. 207—209°), $[\alpha]_D^{16}$ +75·5°±2° in dioxan, and an *isomeride*, prisms, m.p. 150—152°, or hexagonal leaflets, m.p. 150—152° after transformation at 147°; either isomeride is converted by PCl_5 in C_6H_6 at 50° followed by ozonolysis into androstan-3(β)-ol-17-one. A similar change cannot be effected starting from 21-benzylidenepregnane-3(α) : 12(β)-diol-20-one diacetate, m.p. 119—121°, $[\alpha]_D^{16}$ +200·5°±2° in dioxan. H. W.

V.—TERPENES AND TRITERPENOID SAPOGENINS.

Oil of lavender. III. Monoterpene alcohols and acids present as esters in French oil of lavender. C. F. Seidel, H. Schinz, and P. H. Müller (*Helv. Chim. Acta*, 1944, **27**, 663—674).—Fractions, b.p. >100°/11 mm., of French oil of lavender have been examined. The following alcohols have been isolated: *l*-linalool (**I**), b.p. 84—85°/11 mm., α_D −16·8° (phenylurethane, m.p. 61—62°); geraniol (**II**), b.p. 115—116°/14 mm. (allophanate, m.p. 115—116°; 3 : 5-dinitrobenzoate, m.p. 60—61°); nerol (**III**), (diphenylurethane, m.p. 55—62°); *d*-citronellol (**IV**), b.p. 104—105°/11 mm. (allophanate, m.p. 105—106°, $[\alpha]_D$ +2·50° in MeOH); *d*-borneol (**V**), m.p. 203—204°; cumin alcohol (**VI**), b.p. 124°/13 mm. (allophanate, m.p. 184—185°; 3 : 5-dinitrobenzoate, m.p. 96°). (**I**), (**II**), and (**III**) are present in free and esterified forms, (**V**) and (**VI**) only as free alcohol, and (**IV**) only as ester. The identity of (**VI**) is confirmed by the prep. of it (and its derivatives) by reduction of cuminol with $Al(OPr^\beta)_3$ and by its synthesis from C_6H_6 and $Pr^\beta Br$ through *p*-$C_6H_4Pr^\beta Br$ and *p*-$C_6H_4Pr^\beta{\cdot}MgBr$ + CH_2O. The higher fatty acids include *d*-CHMeEt·CO$_2$H, b.p. 75—77°/10 mm., α_D +11° (*thiuronium* salt, m.p. 147—148°, $[\alpha]_D$ +3·6° in MeOH), *n*-$C_5H_{11}{\cdot}CO_2H$ (thiuronium salt, m.p. 154—155°; anilide, m.p. 95—96°), an incompletely identified heptoic acid (thiuronium salt, m.p. 153°), pelargonic acid (thiuronium salt, m.p. 150—151°), tiglic acid, m.p. 63—64°, probably an unsaturated C_8 acid (thiuronium salt, m.p. 150—151°), a monocyclic, singly unsaturated acid, $C_9H_{14}O_2$, hydrogenated to a saturated acid, b.p. 130—135°/10 mm., α_D +3·4° (poorly cryst. anilide; *thiuronium* salt, $C_{17}H_{26}O_2N_2S$, m.p. 154—155°), BzOH, and an unidentified acid, $C_{10}H_{12}O_2$ (possibly a phenylbutyric acid) (*thiuronium* salt, m.p. 184—185°). Coumarin and umbelliferone Me ether are also present. H. W.

New transition from camphor to homocamphor. H. Rupe and C. Frey (*Helv. Chim. Acta*, 1944, **27**, 627—645; cf. A., 1940, II, 136).—The vigorous reaction between CH_2N_2 and camphorquinone gives a mixture from which the solid 4-methoxy-3 : 4-dehydrohomocamphor (**I**), m.p. 54—55°, crystallises, leaving the liquid variety (**II**). (**I**) and (**II**) give *oximes*, m.p. 195—196° and 185—185·5° respectively. Either isomeride is converted by Br in $CHCl_3$ at room temp. into 3-bromo-4-methoxy-3 : 4-dehydrohomocamphor, m.p. 104—105°, and by an excess of Br into 3 : 3-*dibromo*-4-*ketocamphor*, $C_8H_{14}\langle_{CO}^{CO}\rangle CBr_2$ (**III**), m.p. 153—154°. (**II**) does not give homogeneous products with MgEtBr or MgPhBr. Hydrolysis of (**I**) or (**II**) leads to the strongly acidic 4-hydroxy-3 : 4-dehydrohomocamphor (**IV**), m.p. 218—222°, and since the production of a new asymmetric C is excluded it appears that (**I**) and (**II**) are *cis–trans* isomerides, (**I**) being the *trans* variety. (**IV**) and Br in $CHCl_3$ yield 3-*bromo*-4-*hydroxy*-3 : 4-*dehydrohomocamphor*, m.p. 189—191°, whilst (**IV**) and Br vapour yield (**III**). (**IV**) is transformed by *p*-$NO_2{\cdot}C_6H_4{\cdot}COCl$ at 160° into the p-*nitrobenzoate*, m.p. 120—122°, and by boiling EtOH–H_2SO_4 into the *Et ether*, b.p. 142—146°/12 mm., m.p. 70—72°. With $NHPh{\cdot}NH_2$ in EtOH (**IV**) gives a *phenylhydrazone*, m.p. 181° (colourless leaflets or red prisms into which the leaflets slowly pass), but not a di-phenylhydrazone. 4-*Ketohomocamphordioxime* has m.p. 209° (decomp.). (**IV**) is converted by EtO·NO into 4-*keto*-3-*oximinohomocamphor*, m.p. 107—109°. PhCHO (1 mol.) reacts with (**IV**) (2 mols.) in C_5H_5N containing piperidine at 100° or in NaOMe–MeOH to give the *substance*, $C_{20}H_{36}O_4$, m.p. 146—149°. In C_5H_5N–piperidine at room temp. and then at 100°, *p*-$NMe_2{\cdot}C_6H_4{\cdot}CHO$ and (**IV**) afford 4-*keto*-3-p-*dimethylaminobenzylidenehomocamphor*, m.p. 152·5—153°. Under similar conditions *o*-$NO_2{\cdot}C_6H_4{\cdot}CHO$ gives 4-*keto*-3-o-*nitrobenzylidenehomocamphor*, m.p. 140—142° (decomp.), and a *compound*, $C_{29}H_{35}O_8N$. With PhN$_2$Cl (**IV**) yields 4-*ketohomocamphor*-3-*phenylhydrazone*, m.p. 117—118°. (**IV**) is comparatively easily oxidised by $KMnO_4$ to α-*ketoepihomocamphoric acid* (**V**), m.p. 125°, which passes when distilled in a vac. into CO and camphoric anhydride (**VI**). (**V**) gives a p-*nitrobenzylthiuronium* salt, m.p. 181—182°, and a *dinitrophenylhydrazone*, m.p. 192—193° (decomp.). (**V**) is reduced (Na–Hg) to α-*hydroxyepihomocamphorolactone*, m.p. 202—204° (*monohydrate*, m.p. 171—173°, softens at 150°; p-*nitrobenzylthiuronium* salt, m.p. 171—172°). (**VI**) is obtained by oxidation of (**IV**) with CrO_3. (**IV**) is hydrogenated (Ni in dil. EtOH containing Na_2CO_3 at room temp.) to 3 : 4-*dehydrohomocamphor* (**VII**), m.p. 173—175° (*oxime*, m.p. 143·5—145°; *dinitrophenylhydrazone*, m.p. 181—184°). With Br in $CHCl_3$ (**VII**) gives 3 : 4-*dibromohomocamphor*, m.p. 103° (decomp.). Hydrogenation (Ni) of (**VII**) leads to homocamphor (**VIII**), m.p. 192—193° (oxime, m.p. 165°; dinitrophenylhydrazone, m.p. 232—233°). Hydrogenation (H_2 at 60—70°/90 atm., Ni in aq. EtOH) of (**IV**) gives (**VII**) and a dimeric *compound*, m.p. 276—279°. (**IV**) is not hydrogenated in presence of Pd–C, with Na–Hg, or with Zn and AcOH; Clemmensen reduction affords non-homogeneous products. (**IV**) is transformed by NH_2Me at 100° and later at 140—150° into 4-*methylamino*-3 : 4-*dehydrohomocamphor* [*nitrosoamine*, m.p. 167° (decomp.); *picrate*, m.p. 178—180°], obtained similarly but less advantageously from (**II**). Vals. of $[\alpha]^{20}$ in C_6H_6 for (**I**), (**II**), (**IV**), (**VII**), and (**VIII**) are recorded. H. W.


(I.)

Sesquiterpenes. LXIII. Alcohols, hydrocarbons, and oxides of the sesquiterpene series from French oil of lavender. C. F. Seidel, P. H. Müller, and H. Schinz (*Helv. Chim. Acta*, 1944, **27**, 738—747).—The following have been isolated from a fraction (2·7 kg.), b.p. >100°/11 mm., from 19·25 kg. of French oil of lavender: a probably primary, possibly *sec.*, probably tricyclic *alcohol*, $C_{15}H_{24}O$, b.p. 96°/0·07 mm., occurring in the free form and giving a poorly cryst. *allophanate*, m.p. 183—187°; an unesterified monocyclic primary *alcohol*, $C_{15}H_{26}O$, b.p. 107°/0·07 mm., α_D −25·6°, hydrogenated (PtO_2 in EtOAc) to a H_4-*alcohol*, b.p. ~100°/0·04 mm., which is saturated towards $C(NO_2)_4$, oxidised to an aldehyde, b.p. 100—110°/0·04 mm. (non-cryst. semicarbazone and 2 : 4-dinitrophenylhydrazone), and gives a small amount of CH_2O when ozonised; a primary dicyclic *alcohol* (**I**), $C_{15}H_{24}O$, b.p. 100—105°/0·04 mm., α_D −66·96° (*allophanate*, m.p. 188—189°), which is hydrogenated to a H_4-compound (*allophanate*, m.p. 178—179°), oxidised to an

aldehyde, b.p. 95—100°/0·05 mm.; a tricyclic *diol*, $C_{15}H_{28}O_2$, m.p. 150—151° (present as an ester), saturated towards $C(NO_2)_4$ and Br–CS_2 and indifferent to PtO_2 in AcOH, found in the residues from (I); free cadinol (II), identified as cadinene dihydrochloride; free bisabolol containing 5% of (II); caryophyllene, identified as the dihydrochloride and as caryophyllene alcohol; cadinene (III), identified as the dihydrochloride; bisabolene (IV), identified as the trihydrochloride; a dicyclic, cryst. *oxide*, $C_{15}H_{24}O$, m.p. 62—63°, $[\alpha]_D$ −67·85° in $CHCl_3$, hydrogenated (PtO_2 in EtOAc) to a saturated *oxide*, $C_{15}H_{26}O$, b.p. 140—141°/11 mm., and separated from the hydrocarbons by adsorption on SiO_2 gel; cedrene could not be identified. Dehydrogenation of hydrocarbon fractions containing (III) and (IV) by Se at 340° gives cadalene (V) and 1 : 6-$C_{10}H_6Me_2$ (VI). To check the possibility of the production of (VI) by elimination of Pr$^\beta$ from (V), *iso*zingiberene [a hydrocarbon allied to (III)] is dehydrogenated at various temp. Some (VI) is invariably produced in addition to (V), the yield increasing with increasing temp. of dehydrogenation. At 380° the elimination of Pr$^\beta$ is complete so that (V) can no more be detected. H. W.

Isolation of partheniol, parthenyl cinnamate, and other constituents from guayule resin. E. D. Walter (*J. Amer. Chem. Soc.*, 1944, **66**, 419—421).—An Et_2O extract of the exudate of *Parthenium argentatum*, Gray, in 80% alcohol deposits *parthenyl cinnamate* (~20%) (photomicrograph), m.p. 125—126°, also obtained in similar yield by keeping a $COMe_2$ extract of guayule rubber (cf. Alexander, A., 1911, i, 897). Hydrolysis of the ester yields cinnamic acid and *partheniol*, $C_{15}H_{26}O$, m.p. 131° (photomicrograph), which yields no 3 : 5-dinitrobenzoate or phenylurethane and in 90% HCO_2H at room temp. gives a *formate*, b.p. 215° (decomp.)/755 mm. Crystallo-optical properties of the alcohol are reported. Air-dried foliage or the whole shrub yields to warm $COMe_2$ a resin including ~0·25% of a *wax* (C 80·18, H 13·25%), m.p. 76°, which is also obtained from rubber from the retted or unretted shrubs. The alcohol and acid are also obtained by hydrolysing $COMe_2$ extracts of the rubber from retted or whole shrubs or of the foliage, yields of the alcohol being ~2·5%, ~2%, and <1%, respectively. Steam-distilling a $COMe_2$ extract of the rubber gives an oil, b.p. 244—245°/750 mm., $[\alpha]_D$ −17·92°; distilling the resin in vac. gives cinnamic acid and fractions varying from b.p. 70—78°/1 mm., $[\alpha]_D^{22}$ −10·5°, to a *sesquiterpene*, b.p. 246—247°/755 mm., $[\alpha]_D^{22}$ −6·84°. This hydrocarbon may have been formed by dehydration of partheniol. R. S. C.

Triterpenes. LXXXVII. Transformation products of lanosterol. L. Ruzicka, E. Rey, and A. C. Muhr (*Helv. Chim. Acta*, 1944, **27**, 472—489).—Lanosterol (I) contains an unsaturated side-chain with at least 4 C which terminates in the :CMe_2 group. In structure of this side-chain and in behaviour of the part of the mol. which contains the non-reactive double linking. (I) is identical with elemadienolic acid. The unsaponifiable matter of the wool fat of sheep is extracted with $COMe_2$ and the fatty alcohols are removed chromatographically. The mixture is freed from cholesterol by repeated treatment with boiling MeOH. Chromatographic methods of separating the "*iso*cholesterol" (II) thus obtained are less satisfactory than the older acetate method, which leads to the following substances: lanosteryl acetate (III), m.p. 113·5—114·5°, $[\alpha]_D^{14}$ +55·2°, hydrolysed to (I), m.p. 140—141°, $[\alpha]_D^{15}$ +58·2° (*benzoate*, m.p. 191°; 3 : 5-*dinitrobenzoate*, m.p. 201°); dihydrolanosteryl acetate, (IV), m.p. 122—123°, $[\alpha]_D^{20}$ +60·3°, hydrolysed to dihydrolanosterol, m.p. 142·5—143·5°, $[\alpha]_D^{20}$ +60·9°; γ-lanosteryl acetate (V), m.p. 168·5—169·5°, $[\alpha]_D^{16}$ +85·9°, whence γ-lanosterol (VI), m.p. 156—157·5°, $[\alpha]_D^{16}$ +66·2°; agnosteryl acetate, m.p. 174—176°, $[\alpha]_D^{15}$ +88·3°, hydrolysed to agnosterol, m.p. 163·5—164·5°, $[\alpha]_D^{20}$ +76·9°. The main product of the dehydrogenation of (II) by Se at 350° is 1 : 7 : 8-trimethylphenanthrene; a homologue which could not be obtained pure appears to be also present with a *hydrocarbon*, (?) $C_{20}H_{20}$, m.p. 237·5—238·5°, which appears to be a homologue of chrysene according to its absorption in the ultra-violet. Ozonisation of (III) and subsequent fission of the ozonide by boiling H_2O gives $COMe_2$ (identified as the *p*-nitrophenylhydrazone) and, after methylation, *Me acetyltrinorlanosterate*, m.p. 168—170°, hydrolysed to *trinorlanosteric acid*, m.p. 257·5—259·5° (*Me* ester, m.p. 152·5—154·5°). The readily hydrogenated double linking of (I) is therefore present in :CMe_2. (IV) is oxidised by CrO_3 in AcOH at 40° to αβ-unsaturated *ketodihydrolanosteryl acetate*, m.p. 151·5—152·5°, or if introduced into a bath at 146° gives an immediate turbid melt which becomes transparent at 157°, $[\alpha]_D^{16}$ +18·2°, also obtained by ozonisation of (IV), and *diketodihydrolanosteryl acetate*, m.p. 156·5—158·8° and 160·5° after re-solidification, $[\alpha]_D^{16}$ +90·5° [also obtained from (V)], which is unaffected by N_2H_4,H_2O in EtOH at 180° or by boiling Ac_2O but is hydrolysed to *diketodihydrolanosterol*, m.p. 113—115°, $[\alpha]_D^{6}$ +78·3°. This, like (V), is oxidised to *diketodihydrolanostenone*, m.p. 105—107°, $[\alpha]_D^{16}$ +172·6°, reduced (Wolff–Kishner) to a yellow oil. A compound, m.p. 186·5—188·5°, probably *triketodihydrolanosteryl acetate*, is described. Dihydrolanostenone is transformed by NaOEt and amyl formate in MeOH into *hydroxymethylenedihydrolanostenone*, m.p. 124—126° (not const.), which gives a violet colour with $FeCl_3$ and a yellow colour with $C(NO_2)_4$. It is smoothly oxidised by H_2O_2 in alkaline solution to the dicarboxylic *acid*, $C_{30}H_{50}O_4$, m.p. 194·5—196°, $[\alpha]_D^{20}$ +86·7° (non-cryst. *Me*$_2$ ester), which passes at 280—310°/vac. of H_2O pump into *nordihydrolanostenone*, m.p. 113·5—115°, $[\alpha]_D^{20}$ +124·8° [*oxime*, m.p. 202° (decomp.)]. Dihydrolanostenone, m.p. 118—119°, $[\alpha]_D^{18}$ +70·2°, gives an *oxime*, m.p. 169—171°, and a *semicarbazone*, m.p. 236—238° (vac.; decomp.), which is converted by NaOEt–EtOH at 180° into *dihydrolanostene*, $C_{30}H_{52}$, m.p. 72·5—73·5°, $[\alpha]_D^{16}$ +104°, which gives an intense yellow colour with $C(NO_2)_4$; it is transformed by HCl in $CHCl_3$ into *isodihydrolanostene*, m.p. 79·5—80·5°, $[\alpha]_D^{15}$ +36°. (VI) is dehydrogenated (Cu powder) to γ-lanostenone, m.p. 128—129°, $[\alpha]_D^{16}$ +45·6° (oxime, m.p. 188·5—190·5°), converted through the semicarbazone, m.p. 222—225°, into *γ-lanostene*, m.p. 93—94·5° $[\alpha]_D^{15}$ +75·5°. M.p. are corr. and, unless otherwise stated, observed in open capillaries. $[\alpha]_D$ are in $CHCl_3$. H. W.

Triterpene group. XI. Non-saponifiable matter of *Lactucarium germanicum*. J. C. E. Simpson (*J.C.S.*, 1944, 283—286).—The non-saponifiable matter of *L. germanicum* is shown to be a complex mixture of triterpene alcohols; the substances, lactucerin, lactucon, α- and β-lacturerol, and α- and β-lactucol, isolated by previous workers were mixtures. Taraxasterol, β-amyrin, and a monohydric alcohol, *germanicol*, $C_{30}H_{50}O$, m.p. 176—177°, $[\alpha]_D^{17}$ +5·8° (*acetate*, m.p. 274—276°, $[\alpha]_D^{20}$ +18·1°; *benzoate*, m.p. 269—270°, $[\alpha]_D^{19}$ +39·0°), have been isolated. Rotations are in $CHCl_3$. F. R. S.

VI.—HETEROCYCLIC.

Configuration of α-βζ-epoxy-Δ$^\gamma$-heptene-γ-carboxylic [2 : 6-dimethyl-5 : 6-dihydro-1 : 2-pyran-3-carboxylic] acid. M. Delepine and G. Amiard (*Compt. rend.*, 1942, **215**, 309—312; cf. A., 1942, II, 248).—Decarboxylation of the βζ-epoxyheptane-γ-carboxylic acids could not be effected by prolonged heating alone or with Raney Ni or in quinoline containing Cu chromite at 250°, the only observed result being the transformation of the isomeride, m.p. 92°, into that of m.p. 89°. *dl*-2 : 6-Dimethyl-5 : 6-dihydro-1 : 2-pyran-3-carboxylic acid is decarboxylated by Cu chromite–quinoline at 250° to dl-2 : 6-*dimethyl*-5 : 6-*dihydro*-1 : 2-*pyran*, b.p. 115—117°/atm. pressure. Similarly the *d*-acid (I) affords (+)-2 : 6-*dimethyl*-5 : 6-*dihydro*-1 : 2-*pyran* (II), $[\alpha]_D$ +49·7° or +41·1° in Et_2O. The possibility that (I) is intermediately isomerised to 2 : 6-dimethyl-5 : 6-dihydro-1 : 4-pyran-3-carboxylic acid is excluded by the observation that this acid (*l*-form) is decarboxylated to (−)-2 : 6-*dimethyl*-5 : 6-*dihydro*-1 : 4-*pyran* (III), $[\alpha]_D$ −73·5°. (III) (*dl*-form) is transformed by H_2O at 75° into heptan-β-ol-ζ-one (*semicarbazone*, m.p. 105°, or *dihydrate*, m.p. 62°), whilst the optically active material gives an active *keto-alcohol*, $[\alpha]_D$ ~−1·6° (anhyd. *semicarbazone*, m.p. 103°, $[\alpha]_D$ −15° in H_2O). Under similar conditions there is no reaction with (II). Hydrogenation (PtO_2 in Et_2O) of the unsaturated compounds leads to dl-, b.p. 114°/762 mm., and (+)-, b.p. 113·5—115°, $[\alpha]_D$ +0·53°, -2 : 6-*dimethyltetrahydropyran*. Evidence of the reality of the optical activity is afforded. H. W.

Synthetic experiments in the benzpyrone series. VIII. Transformations of 5-hydroxycoumarin derivatives. B. Krishnaswamy, K. R. Rao, and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1944, **19**, **A**, 5—13; cf. A., 1942, II, 170).—5-Hydroxy-4 : 7-dimethylcoumarin (I), obtained from orcinol and $CH_2Ac{\cdot}CO_2Et$ in conc. H_2SO_4 at room temp. (overnight) or 100° (1 hr.) or in HCl–EtOH, is converted by $CH_2{:}CH{\cdot}CH_2Br$ and K_2CO_3 in boiling $COMe_2$ into the *allyl ether*, m.p. 127—128°, which at 160—165° gives 5-*hydroxy*-4 : 7-*dimethyl*-6-*allylcoumarin* (II), m.p. 178—179°, at 195—200° gives 4 : 7-*dimethyl*-Δ$^{2'}$-*dihydropyrano*-2′ : 3′-5 : 6-*coumarin* (III), m.p. 164—165°, and at 225—230° gives (III) and a small amount of 5-*hydroxy*-4 : 7-*dimethyl*-8-*allylcoumarin*, m.p. 239—240°. The structure of (II) is proved by conversion into (III) at 215—220°. In MeOH, (II) gives a $HgCl_2$ additive compound, m.p. 228—229°, converted by aq. KI–I at 100° into 4 : 7-*dimethyl*-5′-*iodomethyl*-, m.p. 166—167°, and thence (Na–EtOH) 4 : 7 : 5′-*trimethyl*-Δ$^{2'}$-*dihydrofurano*-2′ : 3′-5 : 6-*coumarin*, m.p. 205—206°. The difference of this compound from (III) proves the ring-structure of (III). 7-*Allyloxy*-5-*methylcoumarin* (prep. as above), m.p. 78—79°, at 200—205° or, less well, 230—240° gives 7-*hydroxy*-5-*methyl*-8-*allylcoumarin*, m.p. 174—175°. The acetate, m.p. 199—200° (lit. 195°), of (I) with $AlCl_3$ at 130—170° gives 5-*hydroxy*-6-*acetyl*-4 : 7-*dimethylcoumarin*, m.p. 177—178°. The result of Fries rearrangement in the coumarin series depends on the nature and position of substituents and on the experimental conditions. R. S. C.

Azo-dye formation by 5-hydroxycoumarins. S. Rangaswami and K. R. Rao (*Proc. Indian Acad. Sci.*, 1944, **19**, **A**, 14—16).—With 1 mol. of *p*-$NO_2{\cdot}C_6H_4{\cdot}N_2Cl$ at 0° 5-hydroxy-7-methyl- or -4 : 7-dimethylcoumarin in NH_3–EtOH–H_2O or 7-hydroxy-5-methylcoumarin in aq. Na_2CO_3 gives monoazo-*dyes*, but with >2 mols. gives mixed mono- and bis-azo-dyes. R. S. C.

Anthochlor pigments. V. Pigments of *Coreopsis grandiflora*, Nutt. II. T. A. Geissman and C. D. Heaton (*J. Amer. Chem. Soc.*, 1944, **66**, 486—487; cf. A., 1943, II, 274).—5 : 6-Dimethoxy-2-coumaranone [prep. from 3 : 4 : 5 : 1-$(OH)_3C_6H_2{\cdot}CO{\cdot}CH_2Cl$ by Me_2SO_4–

Na_2CO_3–H_2O), m.p. 122—123°, and 3 : 4 : 1-$(OMe)_2C_6H_3$·CHO (**I**) in warm NaOH–EtOH–H_2O give 5 : 6 : 3′ : 4′-tetramethoxybenzylidene-2-coumaranone (84%), m.p. 156—157°, identical with leptosidin Me_3 ether. 3 : 4 : 5 : 1-OH·C_6H_2(OMe)$_2$·COMe and (**I**) in warm NaOH–EtOH–H_2O give 2 : 3 : 4-OH·$C_6H_2(OMe)_2$·CH:CH·$C_6H_3(OMe)_2$-3 : 4, m.p. 121—122° (lit. 119°), cyclised in boiling HCl–EtOH–H_2O to 7 : 8 : 3′ : 4′-tetramethoxyflavanone, m.p. 143·5—144° (and a small amount of another substance), identical with the Me_2 ether of the naturally occurring flavanone. R. S. C.

Synthesis of hibiscetin. P. R. Rao, P. S. Rao, and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1944, **19**, **A**, 88—92).—2 : 6 : 1 : 4-$(CH_2Ph·O)_2C_6H_2(OMe)_2$ with OMe·CH_2·CN, $ZnCl_2$, and HCl in Et_2O and then H_2O at 100° gives 2 : 6-dihydroxy-3 : 6 : ω-trimethoxyacetophenone (**I**), m.p. 150—151°, by way of its semi-solid ketimine ydrochloride (formed with a by-product, m.p. 110—112°). The $ZnCl_2$ is responsible for the hydrolysis, since this does not occur in absence of $ZnCl_2$. 3 : 4 : 5 : 1-$(OMe)_3C_6H_2$·CO_2Na, [3 : 4 : 5 : 1-$(OMe)_3C_6H_2$·CO]$_2$O, and (**I**) at 175—180°/vac. give a moderate yield of 7-*hydroxy*-3 : 5 : 8 : 3′ : 4′ : 5′-*hexamethoxyflavone*, m.p. 238—240°, whence Me_2SO_4–NaOH yields hibiscetin Me_7 ether, hydrolysed by boiling HI–Ac_2O to hibiscetin (A., 1942, II, 327). R. S. C.

Constitution of belmacamgenin and belmacamdin. S. Wang and M. Hu (*J.C.S.*, 1944, 307).—From the powdered root of *Belmacamda*, there has been isolated belmacamdin (**I**), m.p. >300°, which is hydrolysed (HCl–EtOH) to belmacamgenin (**II**), m.p. 227°, and glucose. (**II**) is probably a pentahydroxymonomethoxy*iso*flavone and it forms an Ac derivative, m.p. 184—185°, and Me_2 ether, m.p. 162°. Methylation of (**I**) followed by hydrolysis (HCl–EtOH) yields a compound, m.p. 165°, identical with 7 : 3′-dimethylirigenin F. R. S.

Oxidation of catechin to cyanidin : applications of the reaction. J. Lavollay and M. Vignau (*Compt. rend.*, 1943, **217**, 86—88).—Oxidation of catechin (**I**) to cyanidin is effected, without protecting the OH groups (cf. Appel *et al.*, A., 1935, 757), by adding $Fe_2(SO_4)_3$, $K_3Fe(CN)_6$, CuO, MnO_2, $KClO_3$, $NaBO_3$, or $K_2S_2O_8$, in conc. H_2SO_4 to (**I**) in $COMe_2$; the diluted mixture is extracted with *iso*-C_5H_{11}·OH. Possible applications of the reaction are discussed. A. T. P.

Auroxanthin. II. P. Karrer and J. Rutschmann (*Helv. Chim. Acta*, 1944, **27**, 320).—Auroxanthin, m.p. 203°, obtained in very small amount from the blossoms of the yellow pansy, is $C_{40}H_{56}O_4$. Micro-hydrogenation indicates the presence of 9 double linkings. Acetylation (Ac_2O in C_5H_5N) appears to cause profound changes. H. W.

Dioxans.—See B., 1944, II, 157.

Reactions of anthocyanins with molybdate. H. Blaschko (*Proc. Biochem. Soc.*, 1944, **38**, xxxii—xxxiii).—Colour develops only on addition of NH_4 molybdate to solutions in 1% HCl of anthocyanins that contain free vicinal OH groups, *e.g.*, cyanidin and delphinidin. P. G. M.

Thiochroman derivatives with tocopherol structure. P. Karrer and P. Leiser (*Helv. Chim. Acta*, 1944, **27**, 678—684).—*m*-2-Xylenol is converted by H_2SO_4,H_2O at 100—110° into 1 : 2 : 6 : 4-OH·$C_6H_2Me_2$·SO_3Na, which with $ClCO_2Et$ and NaOH affords *Na* O-*carbethoxy*-2 : 6-*dimethylphenol*-4-*sulphonate*. The corresponding *sulphonyl chloride*, m.p. 127°, is reduced by Zn dust and HCl in EtOH to 4-*thiol*-2 : 6-*dimethylphenol* (**I**), m.p. 86°. This with phytol in boiling HCO_2H yields 6-hydroxy-5 : 7-dimethyl-2-δθμ-trimethyltridecylthiochroman (5 : 7-dimethylthiotocol), isolated as the *acetate* (**II**), b.p. 190—205°/0·001 mm. Condensation of (**I**) with CMe_2:CH·CH_2·OH [prep. from CMe_2:CH·CHO and Al(OPr$^\beta$)$_3$ described] gives 6-*hydroxy*-2 : 2 : 5 : 7-*tetramethylthiochroman* (**III**), b.p. 120—125°/0·002 mm. Trimethyl-*p*-benzoquinonemonoxime, m.p. 182°, is reduced ($Na_2S_2O_4$ in hot EtOH) to 4 : 2 : 3 : 6 : 1-NH_2·C_6HMe_3·OH, which affords 2 : 3 : 6 : 1-$C_6H_2Me_3$·OH when diazotised and heated with Zn dust. This yields 1 : 2 : 3 : 6 : 4-OH·C_6HMe_3·SO_3Na, converted by $ClCO_2Et$ and NaOH into *Na* O-*carbethoxy*-2 : 3 : 6-*trimethylphenol*-4-*sulphonate* (+1H_2O). The corresponding *sulphonyl chloride* gives 4-*thiol*-2 : 3 : 6-*trimethylphenol*, m.p. 87° (Pb salt), which yields 6-*hydroxy*-5 : 7 : 8-*trimethyl*-2-δθμ-*trimethyltridecylthiochroman* (**IV**), b.p. 215—225° (bath)/0·001 mm. (**II**), (**III**), and (**IV**) like the tocopherols have marked reducing power and are oxidised by $FeCl_3$, $AuCl_3$, or $AgNO_3$. With $FeCl_3$ in presence of 2 : 2′-dipyridyl they appear to require 3 equivs. of oxidising agent probably on account of the conversion of thiol into disulphide. Oxidation with $AuCl_3$ is apparently not homogeneous. (**II**) is without vitamin-*E* action and is not antagonistic to α-tocopherol acetate. H. W.

Pyrolysis of xanthopinacol and related compounds. A. Schönberg and A. Mustafa (*J.C.S.*, 1944, 305—306).—When heated in CO_2, xanthhydrol gives H_2O, xanthen (**I**), and xanthone (**II**); dixanthhydryl ether forms (**I**) and (**II**); xanthopinacol affords H_2O, (**I**) and (**II**), and thioxanthhydrol yields thioxanthen, thioxanthone, and dithiodixanthylen. F. R. S.

Synthesis of compounds of the indole and trimethylenepyrrole type. Buu-Hoï and P. Cagniant (*Compt. rend.*, 1943, **217**, 26—28).—ω-Δ^2-cyclo*Pentenyl*-ωω-*dimethylacetophenone*, b.p. 165—168°/12 mm., or -ω-*methyl*-ω-*ethyl*-, b.p. 180—182°/10 mm., or -ω-*methyl*-ω-*benzylacetophenone*, b.p. 232—235°/10 mm. (from ω-Δ^2-cyclo*pentenyl*-ω-*methylacetophenone*, b.p. 158—160°/10 mm., and BzCl), is converted by $NaNH_2$ in boiling PhMe into 4 : 5-*trimethylene*-3 : 3-*dimethyl*-, m.p. 89—90°, b.p. 158—162°/13 mm., -3-*methyl*-3-*ethyl*-, b.p. 180—182°/12 mm., and -3-*benzyl*-3-*methyl*-2-*pyrrolidone*, b.p. 232—236°/9 mm., respectively. With the last-named compound, some β-Δ^1-cyclo*pentenyl*-γ-*phenylpropane*, b.p. 137—140°/10 mm., is isolable. ω-Δ^2-cyclo*Hexenyl*-ωω-*dimethylacetophenone*, b.p. 182—185°/14 mm., gives 2-*keto*-3 : 3-*dimethyloctahydroindole*, m.p. 127·5—128°. Δ^2-cyclo*Pentenylphenylacetonitrile*, b.p. 165—168°/10 mm., obtained from Δ^2-chloro*cyclo*pentane and CH_2Ph·CN (Na), is converted (Na derivative) by Ph·$[CH_2]_2$·Br into Δ^2-cyclo*pentenophenyl*-β-*phenylethylacetonitrile*, b.p. 202—205°/0·5 mm. CH_2:CH·CH_2·CO_2H gives an amide, m.p. 94°, not cyclised by $NaNH_2$ in boiling PhMe. No analyses of the compounds are given. A. T. P.

Synthetic analgesics. I. Synthesis of basic benzofuran derivatives and certain 4-phenylpiperidine compounds. F. Bergel, J. W. Haworth, A. L. Morrison, and H. Rinderknecht. **II. New synthesis of pethidine and similar compounds.** F. Bergel, A. L. Morrison, and H. Rinderknecht. **III. Action of hydrogen halides on ethers of αα-bis-(β′-hydroxyethyl)phenylacetonitrile.** F. Bergel, A. L. Morrison, and H. Rinderknecht. **IV. Synthesis of 3-substituted piperidines and pyrrolidines.** F. Bergel, N. C. Hindley, A. L. Morrison, and H. Rinderknecht (*J.C.S.*, 1944, 261—265, 265—267, 267—269, 269—272).—I. Acetylpæonol, paraformaldehyde (**I**), and $NHMe_2$,HCl in EtOH give *β-dimethylamino*-2-*acetoxy*-4-*methoxypropiophenone hydrochloride* (**II**), m.p. 175°, hydrolysed (HCl) to the -2-*OH*-compound (**III**), m.p. 166—167°. Similarly pæonol with $C_5H_{11}N$,HCl and (**I**) affords *β-piperidino*-2-*hydroxy*-4-*methoxypropiophenone hydrochloride*, m.p. 188—189°. CH_2BzBr and (**III**) with KOH do not form a coumarone but yield CH_2Bz·NMe_2 with some 2-hydroxy-4-methoxyphenyl vinyl ketone, isolated as the 2 : 4-*dinitrophenylhydrazone*, m.p. 244—245°. Et 5-methoxy-2-acetylphenoxyacetate, (**I**), and $NHMe_2$,HCl give *Et* 2-*β-dimethylaminopropionyl*-5-*methoxyphenoxyacetate* (**IV**), m.p. 149° (-*piperidino*-compound, m.p. 134°), and the corresponding *acid*, m.p. 197° (-*piperidino*-compound, m.p. 183—184°), is similarly prepared. Ac_2O–NaOAc with (**IV**) causes disruption of the mol. Addition of Br in AcOH to (**II**) leads to *α-bromo-β-dimethylamino*-2-*acetoxy*-4-*methoxypropiophenone hydrobromide*, m.p. 161°, of which the -2-*OH*-compound, m.p. 179°, with K_2CO_3–$COMe_2$ affords the unstable 2-dimethylaminomethyl-6-methoxycoumaranone hydrochloride, m.p. 144—145° (*picrate*, m.p. 123—124°; polymeric *substance*, $C_{12}H_{16}O_3NCl$). *o*-Vanillin with CH_2AcCl and KOH–EtOH gives 7-*methoxy*-2-*acetylcoumarone*, m.p. 92°, which with (**I**) and $C_5H_{11}N$,HCl affords 2-*β-piperidinopropionyl*-7-*methoxycoumarone hydrochloride*, m.p. 170—172° (*picrate*, m.p. 158—159°). The *azlactone*, m.p. 167—169°, of 2-benzyloxybenzaldehyde with NaOH in N_2 yields 2-*benzyloxyphenyl-pyruvic acid*, m.p. 119—120°, converted through the oxime into the -*acetonitrile* (**V**), m.p. 75—77°. *o*-CN·C_6H_4·CH_2·CN is similarly obtained from the *azlactone*, m.p. 154—156°, of 2-OMe·C_6H_4·CHO, and 2 · 3-*dimethoxyphenylacetonitrile*, b.p. 158—160°/12 mm., from the *azlactone*, m.p. 167—168°, of 2 : 3-$(OMe)_2C_6H_3$·CHO. (Cl·$[CH_2]_2)_2$NH, $NaNH_2$, and (**V**) in PhMe give 4-(2′-*benzyloxyphenyl*)-1-*methylpiperidine*-4-*nitrile hydrochloride*, m.p. 220—221°, which with HCl (sealed tube) affords the *hydrochloride* of 4-(2′-*hydroxyphenyl*)-1-*methylpiperidine*-4-*carboxylic acid lactone* (+0·5H_2O), m.p. 260—263°. The corresponding acetonitriles yield respectively 4-(2′ : 3′-*dimethoxyphenyl*)-1-*methylpiperidine*-4-*nitrile*, m.p. 107—110°, and 4-(2′-*hydroxy*-3′-*methoxyphenyl*)-1-*methylpiperidine*-4-*carboxylic acid lactone*, m.p. 115—117°, and 4-(2′-*methoxyphenyl*)-1-*methylpiperidine*-4-*nitrile*, m.p. 97—99°, which with MgMeI affords 4-*acetyl*-4-(2′-*methoxyphenyl*)-1-*methylpiperidine* (**VI**) (picrate, m.p. 197—200°). 4-Acetyl-4-phenyl-1-methylpiperidine with Na–EtOH gives 4-*phenyl*-1-*methyl*-4-(α-*hydroxyethyl*)*piperidine*, m.p. 117—119°. Na–EtOH and (**VI**) yield 2-*methyl*-3-4′-spiro-(1′-*methylpiperidine*)*coumaran* (*picrate*, m.p. 182—184°). 4-Phenyl-1-methylpiperidine-4-nitrile and Na–EtOH form 4-phenyl-1-methylpiperidine (*picrate*, m.p. 239—240°), identical with that obtained by decarboxylation of the corresponding -4-carboxylic acid. 4-(2′-*Hydroxyphenyl*)-, m.p. 179—181°, and 4-(2′ : 3′-*dimethoxyphenyl*)-1-*methylpiperidine*, b.p. 125—127°/1 mm. (*picrate*, m.p. 159—162°), are similarly prepared; the latter is hydrolysed to the (*OH*)$_2$-compound, m.p. 200—205°. γ-*Diethylamino*-α-*phenyl*-α-*ethylbutyronitrile*, b.p. 161—166°/10—12 mm., is similarly reduced to γ-*phenyl*-n-*amyldiethylamine*, b.p. 134°/15 mm. 4-Phenyl-1-methylpiperidine-4-nitrile is reduced (H_2–$PdCl_2$) to *bis*-(4-*phenyl*-1-*methylpiperidyl*-4-*methyl*)*amine*, m.p. 90—93°.

II. CH_2Cl·OMe with $(CH_2)_2O$ and $HgCl_2$ give *Me β-chloroethyl formal*, b.p. 134—139°; *β-chloroethyl Et formal*, b.p. 62—65°/50 mm., is similarly prepared. CH_2Ph·CN with $NaNH_2$ and Cl·$[CH_2]_2$·O·CH:CH_2 affords αα-*bis*-(β′-*vinyloxyethyl*)*phenylacetonitrile* (**VII**), b.p. 125—135°/0·15 mm., hydrolysed (HCl) to αα-*bis*-(β-*hydroxyethyl*)*phenylacetonitrile*, m.p. 96—98° [also obtained by mild acid hydrolysis of αα-*bis*-(β′-*methoxymethoxyethyl*)*phenylacetonitrile*, b.p. 147—155°/0·05—0·1 mm.], which with $SOCl_2$ and $NPhEt_2$ yields the αα-*bis*-(β′-*chloroethyl*) compound, m.p. 52°. This nitrile

condenses with NH_2Me in EtOH (sealed tube) to 4-phenyl-1-methylpiperidine-4-nitrile, which is identical with that obtained by Eisleb's method (cf. *Ber.*, 1942, **75**, 1435), and is hydrolysed to the 4-carboxylic acid. From the acid, the *hydrochlorides* of the *Prα*, m.p. 181—183°, *Prβ*, m.p. 192—195°, *OH·[CH$_2$]$_2$*, m.p. 195—200°, *allyl*, m.p. 155—158°, and cyclo*hexyl* esters, m.p. 234—236°, are prepared; the Et ester is pethidine. A similar series of reactions leads to *αα-bis-(β'-vinyloxyethyl)* b.p. 135—140°/0·1 mm., and *-(β'-hydroxyethyl)-o-tolylacetonitrile*, m.p. 95—100°, 4-(*o*-tolyl)-1-methylpiperidine-4-nitrile [*hydrochloride*, m.p. 279—280°; *picrate*, m.p. 265° (decomp.)], and *Et* 4-(o-*tolyl*)-1-*methylpiperidine*-4-*carboxylate*, b.p. 175°/11 mm. (*hydriodide*, m.p. 175—176°).

III. $CH_2Ph·CN$, $NaNH_2$, and $Br·[CH_2]_2·OEt$ in PhMe give *αα-bis-(β'-ethoxyethyl)phenylacetonitrile*, b.p. 120—123°/0·05 mm., which with aq. HBr (sealed tube) forms *α-phenyl-α-(β'-bromoethyl)-butyrolactone*, b.p. 140—142°/0·2 mm. (*Cl*-compound, an oil), converted by piperidine into the *-piperidino*-compound, b.p. 154°/0·1 mm. (*hydrochloride*, m.p. 217—217°). Aq. HCl and (**VII**) afford *α-phenyl-α-(β'-hydroxyethyl)butyrolactone*, b.p. 172°/0·1 mm. 4-Phenylpentamethylene oxide-4-nitrile and aq. HBr (sealed tube) yield *phenyl-αα-bis-(β'-bromoethyl)acetic acid*, m.p. 118° [also obtained from (**VII**) and HBr], which with EtOH–HCl followed by NH_2Me gives pethidine.

IV. $CH_2Ph·NHMe$ and $Br·[CH_2]_3·Cl$ give *benzylmethyl-γ-chloropropylamine* (**VIII**), b.p. 137—138°/16 mm. $CH_2Ph·CN$ and bromoacetal with $NaNH_2$ in Et_2O afford *β-cyano-β-phenylpropaldehyde diacetal*, b.p. 120—121°/0·2 mm., which is hydrolysed (HCl in N_2) to *β-cyano-β-phenylpropaldehyde*, b.p. 109—111°/0·1 mm. $CH_2Ph·CN$ and benzylmethyl-β-chloroethylamine (**IX**) with $NaNH_2$ yield *γ-benzylmethylamino-α-phenylbutyronitrile*, b.p. 158°/0·1 mm. (*reineckate*, m.p. 104—107°), which is reduced (H_2–C–$PdCl_2$) to 3-*phenyl*-1-*methylpyrrolidine*, b.p. 105—110°/11 mm. (*picrate*, m.p. 155—158°). $CN·CHPh·CO_2Et$ and Na in Et_2O with (**IX**) lead to *Et α-cyano-γ-benzylmethylamino-α-phenylbutyrate*, b.p. 176—178°/0·2 mm., which is hydrogenated to *Et* 3-*phenyl*-1-*methylpyrrolidine*-3-*carboxylate*, b.p. 114°/0·4 mm. (*picrate*, m.p. 115—118°). $CN·CHPh·CO_2Et$ with (**VIII**) and $NaNH_2$ forms *Et α-cyano-δ-benzylmethylamino-α-phenylvalerate*, b.p. 180°/0·2 mm., hydrogenated to *Et* 3-*phenyl*-1-*methylpiperidine*-3-*carboxylate*, b.p. 104°/0·2 mm. (*hydrochloride*, m.p. 177—180°; *hydriodide*, m.p. 207°); the *acid* (*picrate*, m.p. 196—199°) formed by hydrolysis of the preceding ester gives a Me ester (*hydrochloride*, m.p. 177—179°), Prα ester, b.p. 110°/0·2 mm. (*hydrochloride*, m.p. 174—175°), Prβ ester, b.p. 110°/0·2 mm. (*hydrochloride*, m.p. 191—193°), and *diethylamide*, b.p. 125—128°/0·1 mm. *o*-$C_6H_4Me·CH_2·CN$ with $NaNH_2$ and Et_2CO_3 affords *Et* o-*tolylcyanoacetate*, b.p. 110—114°/0·1 mm., which with (**VIII**) and $NaNH_2$ yields *Et α-cyano-δ-benzylmethylamino-α-o-tolylvalerate*, b.p. 199—200°/0·2 mm., hydrogenated to *Et* 3-(o-*tolyl*)-1-*methylpiperidine*-3-*carboxylate*, b.p. 126—128°/0·2 mm. (*hydrochloride*, m.p. 200—201°; *hydriodide*, m.p. 178—180°). Using the appropriate reagents the following are prepared similarly: *Et α-cyano-δ-benzylmethylamino-α-benzylvalerate*, b.p. 225—235°/0·4 mm.; *Et* 3-*benzyl*-1-*methylpiperidine*-3-*carboxylate*, b.p. 125—135°/0·3 mm.; *Et δ-chloro-α-cyano-α-phenylvalerate*, b.p. 128—129°/0·1 mm.; *Et α-cyano-δ-dibenzylamino-α-phenylvalerate*, b.p. 215—217°/0·1 mm.; *Et αγ-*, b.p. 145°/0·1 mm., and *αβ-dicyano-α-phenylbutyrate*, b.p. 141—142°/0·1 mm.; *Et* 3-*phenylpiperidine*-3-*carboxylate*, b.p. 115—117°/0·1 mm. (*NO*-derivative, m.p. 88—89°); and *Et* 3-*phenylpyrrolidine*-3-*carboxylate*, b.p. 97°/0·1 mm. F. R. S.

Tetra- and hexa-hydronicotinic acid as growth-promoting factors for *Staphylococcus aureas* and *Bacillus proteus vulgaris*. H. von Euler, B. Högberg, P. Karrer, H. Salomon, and H. Ruckstuhl (*Helv. Chim. Acta*, 1944, **27**, 382—390).—The isolation of 1 : 2 : 5 : 6-tetrahydronicotinic acid (**I**), its 1-Me derivative, and arecoline from technical residues is described. Me 1 : 2 : 5 : 6-tetrahydronicotinate hydrochloride is converted by $NaNO_2$ and HCl into the NO-derivative of the ester, transformed by liquid NH_3 into 1-*nitroso*-4-*aminopiperidine*-3-*carboxylamide*, m.p. 172° (*hydrochloride*, m.p. 227—228°). (**I**), $ClCO_2Et$, and Na_2CO_3 give 1-*carbethoxy*-1 : 2 : 5 : 6-*tetrahydronicotinic acid*, m.p. 78°, converted by successive treatments with $SOCl_2$ and NH_3–Et_2O into 1-*carbethoxy*-1 : 2 : 5 : 6-*tetrahydronicotinamide*, m.p. 136—137°, from which CO_2Et could not be removed without involving $·CO·NH_2$. (See also A., 1944, III, 616.) H. W.

Heterocyclic ketones. IV. Properties of αα-dihalogeno-derivatives of heterocyclic nitrogen compounds. E. I. Elkina and M. M. Schemjakin (*J. Gen. Chem. Russ.*, 1943, **13**, 301—303).—2 : 2-Dichloro-*N*-methyldihydropyridine (**I**) and the corresponding quinoline derivative react immediately with H_2O to form *N*-methyl-2-pyridone and *N*-methylcarbostyril respectively. (**I**) is converted by liquid NH_3 into 2-imino-*N*-methyldihydropyridine, and by NH_2Ph into the corresponding anilo-derivative. R. C. P.

Oxidation of nicotine to nicotinic acid. N. A. Vasiunina, A. A. Beer, and N. A. Preobrashenski (*J. Appl. Chem. Russ.*, 1943, **16**, 206—210).—5 g. of nicotine (**I**) + 25 ml. of 27% HNO_3 are added dropwise to 180 ml. of 27% HNO_3 at 98°, and the mixture is kept at 98° for 3 hr. (yield 70%). 5 g. of (**I**) + 20 ml. of H_2O are slowly introduced into 20 g. $KMnO_4$ in 80 g. H_2O at 70°, $KMnO_4$ crystals are slowly added to the solution, and the mixture is kept for 1 hr. at 80—85° (yield 80%). 5 g. of (**I**) + 50 ml. of 35% H_2SO_4 are added within 1 hr. to 41 g. of $MnO(OH)_2$ + 100 ml. of 35% H_2SO_4 at 100—105° (yield 75%). J. J. B.

Isolation of the nicotinamide formed from asparagine and glutamic acid. M. R. Bovarnick (*J. Biol. Chem.*, 1944, **153**, 1—3; cf. A., 1944, II, 116).—Pure nicotinamide has been isolated by extraction of the mixture formed by heating solutions of asparagine and glutamic acid with Et_2O, followed by repeated recrystallisation of the extract from C_6H_6. J. Ho.

Nicotinamides.—See B., 1944, II, 157.

Sulphanilamide derivatives. F. S. Spring and E. P. H. Young (*J.C.S.*, 1944, 248—249).—Sulphanilamide derivatives with alkyl attached to N^1 are prepared, to test their tuberculocidal properties, but they are inactive. Adipamide and Br–33% aq. NaOH at 100° (bath), followed by cold *p*-$NO_2·C_6H_4·SO_2Cl$ (**I**) or *p*-$NHAc·C_6H_4·SO_2Cl$ (**II**) in Et_2O, give *NN'-di-*(p-*nitrobenzenesulphonyl*)- (**III**), m.p. 201°, or *NN'-di*(*acetylsulphanilyl*)-*tetramethylenediamine* (**IV**), m.p. 233° (sinters at 218°), respectively. (**III**) is converted by Sn in boiling HCl–EtOH into *NN'-disulphanilyltetramethylenediamine*, m.p. 205° (hydrochloride, m.p. 241°), also obtained from (**IV**) and boiling HCl–EtOH. *n*-$C_{17}H_{35}·NH_2$ and (**I**) in Et_2O yield *heptadecyl*-p-*nitrobenzenesulphonamide*, m.p. 90·5°, converted by Sn–HCl into N^1-n-*heptadecylsulphanilamide*, m.p. 118°, also prepared by hydrolysis of its N^4-*Ac* derivative, m.p. 128°, obtained from (**II**) in Et_2O. 2-*n*-Propylaminopyridine and (**II**) in dry C_5H_5N give N^1-2-*pyridyl*-N^1-n-*propylsulphanilamide*, m.p. 108°. 2-Aminopyridine (**V**) and $NaNH_2$–C_5H_5N, followed by *n*-$C_5H_{11}Br$ (2 days at room temp., then reflux for 3 hr.), yield 2-n-*amylaminopyridine*, m.p. 43°, b.p. 130—135°/12 mm. (*picrate*, m.p. 121°), converted by (**II**) in C_5H_5N into the N^4-*Ac* derivative, m.p. 83°, hydrolysed to N^1-2-*pyridyl*-N^1-n-*amylsulphanilamide*, m.p. 74—75°. 2-Cetylaminopyridine, b.p. 210—220°/12 mm., m.p. 67° (wax) (*picrate*, m.p. 84°); gives, through the N^4-*Ac* derivative, m.p. 88°, and aq. NaOH–EtOH, N^1-2-*pyridyl*-N^1-*cetylsulphanilamide*, m.p. 77°. 2-*Octadecylaminopyridine*, b.p. 180—185°/0·01 mm., m.p. 66—67° (waxy), affords N^1-2-*pyridyl*-N^1-*octadecylsulphanilamide*, m.p. 70—71°. (**V**), $NaNH_2$, and xylene at 100° (bath), then geranyl chloride at 150° for 3 hr., give 2-*geranylaminopyridine*, b.p. 185—190°/12 mm. (*picrate*, m.p. 125°), converted into N^1-*geranyl*-N^1-2-*pyridylsulphanilamide*, m.p. 75—76°. *n*-$C_{16}H_{33}Cl$, 6-amino-2-methylpyridine, and $NaNH_2$ (2 days) yield 2-*octadecylamino*-6-*methylpyridine*, b.p. 205°/0·25 mm., m.p. 46° (*picrate*, m.p. 101°), which gives, through the N^4-*Ac* derivative, m.p. 84°, N^1-2-(6-*methylpyridyl*)-N^2-*octadecylsulphanilamide*, m.p. 77—78°. A. T. P.

Synthesis of *dl*-tryptophan. H. R. Snyder and C. W. Smith (*J. Amer. Chem. Soc.*, 1944, **66**, 350—351).—$CH_2(CO_2Et)_2$ with, successively, $NaNO_2$–H_2O–AcOH at 20°, H_2–Pd–C–EtOH at 1500 lb., and Ac_2O–EtOH gives $NHAc·CH(CO_2Et)_2$, the Na derivative of which, when treated with 3-indolylmethyltrimethylammonium iodide (**I**) (A., 1944, II, 234) in xylene–dioxan at 92°, raised gradually to 125°, gives *Et α-acetamido-α-carbethoxy-β-3-indolylpropionate*, m.p. 158°. Hot aq. NaOH then gives the corresponding *NHAc-acid*, m.p. 144·5° (decomp.), which in boiling H_2O gives acetyl-*dl*-tryptophan and thence, by hot aq. acid, *dl*-tryptophan, the yield being ~45% calc. on the indole used to prepare (**I**). R. S. C.

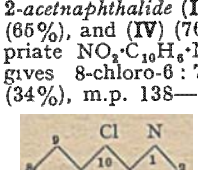
Synthesis of tryptophan. N. F. Albertson, S. Archer, and C. M. Suter (*J. Amer. Chem. Soc.*, 1944, **66**, 500).—3-Indolyldimethylethylammonium iodide with $CRNa(CO_2Et)_2$ (R = H, NHAc, or NHBz) (cf. Snyder, A., 1944, II, 234) gives Et α-carbethoxy-β-3-indolylpropionate, *α-acet-*, m.p. 157°, and *α-benz-amido-α-carbethoxy-β-3-indolylpropionate*, m.p. 142°, and thence the derived dicarboxylic *acids*, m.p. 187—189°, 135—137° (decomp.), and 85—90° (decomp.), respectively, and by decarboxylation (180—200°) thereof β-3-indolylpropionic acid, m.p. 128—130°, and its α-NHAc- and α-NHBz-derivatives, whence tryptophan is obtained in yields up to 35% calc. on the indole used. R. S. C.

Isatin and ammonia. III. Enlargement of the isatin into the quinazoline ring. G. Jacini (*Gazzetta*, 1943, **73**, 85—88; cf. A., 1944, II, 234).—Isatin-3-anil and similar compounds in 10% NaOH with 20% aq. NH_3 and H_2O_2 give 3-*phenyl-*, m.p. 276°, 3-o-*tolyl-*, m.p. 246°, 3-p-*aminophenyl-*, m.p. 311°, 3-p-*anisyl-*, m.p. 229°, and 3-α-*naphthyl*-2 : 4-*diketotetrahydroquinazoline*, m.p. 268°. *Isatin*-3-p-*anisylimide* has m.p. 229°. E. W. W.

Condensations with Michler's ketone (formation of dyes). H. L. Kehlstadt (*Helv. Chim. Acta*, 1944, **27**, 685—701).—The condensation of $CO(C_6H_4·NMe_2$-$p)_2$ (**I**) with 2-methylquinoline (**II**) and analogous substances and the reactions of the product with organo-metallic compounds are described. (**I**), (**II**), and $AlCl_3$ at 170° yield *αα-di-pp'-tetramethyldiaminodiphenyl-β-2-quinolylethylene* (**III**), m.p. 178—179°; condensation with $ZnCl_2$ is less satisfactory. The presence of unchanged (**I**) in (**III**) can be detected by the formation of an

immediate blue colour when a solution of (I) is reduced by Na–Hg and then acidified (AcOH). (III) is yellow but becomes orange when exposed to sunlight. (III) gives strongly coloured salts involving the ring N and nearly or completely colourless salts involving the N in NMe_2. There are obtained the yellowish *triperchlorate*, decomp. 238°, red *monoperchlorate*, m.p. 238°, dark *monopicrate*, m.p. 200° (decomp.), *styphnate*, almost colourless, very unstable hydrochloride, and a dark red, non-hygroscopic, cryst. *hydrochloride*, m.p. 210°, *methiodide*, decomp. 170°, *ferrocyanide*, and an *adduct* with Me_2SO_4. (III) dyes mordanted cotton in brownish-red shades. (I), (II), and $NaNH_2$ at 140—150° give 2-*quinolylmethyldi*-pp-*tetramethyldiaminodiphenylcarbinol* (IV), m.p. 187°, becomes yellow. (IV) is not readily converted into a dye. It is stable towards cold mineral acids, gives a colourless, cryst. *perchlorate*, m.p. (indef.) 180°, and can be cryst. Short warming with org. acids, preferably HCO_2H, leads to pure (III). MgPhBr could not be added to (III). LiPh and highly purified (III) yield a product which, after decomp. with dil. acid, gives a green solution resembling malachite-green (V) and darkening when heated. It appears definite that the addition of the third Ph leads to a system in which the tenaciousness of the Ph residues is inadequate so that appreciable if not considerable hydrolysis to $OH{\cdot}CPh(C_6H_4{\cdot}NMe_2)_2$ occurs. Attempts to determine the (V) which is formed lead to the disclosure that union with LiPh is never complete. (V) cannot be separated by crystallisation and iodometric, titanometric, colorimetric, and chromatographic assays are unsatisfactory, but (V) can be determined by treatment with NH_3 in $CHCl_3$, alcoholysis of the product, and titration of the NH_3 produced. An optical method is also described. (III) is reduced (H_2 at 70—80°/120 atm.; Ni in EtOAc–EtOH–H_2O) to *αα-di*-pp′-*tetramethyldiaminodiphenyl-β*-1 : 2 : 3 : 4-*tetrahydro*-2-*quinolylethane* (VI), m.p. 106—107°, which gives colourless salts (very hygroscopic *hydrochloride*, m.p. 190°) and with $CH_2Br{\cdot}CO_2Et$ a material, decomp. 100—110°. As *sec.* base it affords a *Bz* derivative, m.p. 153—154°, and a *NO-amine*, but it could not be acetylated. The amorphous, hygroscopic *methiodide*, m.p. 154—156°, and yellow *picrate*, softens 148—158°, are described. (VI) is readily oxidised by PbO_2 or chloranil but the dark green-blue product is not a dye. (I) and $CH_2Ph{\cdot}MgCl$ in C_6H_6 afford α-phenyl-ββ-di-pp′-tetramethyldiaminodiphenylethylene (VII), m.p. 131°, which gives a dark blue-green solution in AcOH becoming colourless on addition of mineral acid. (VII) yields a colourless *hydrochloride*, m.p. 190—192°, a yellow *picrate*, m.p. 182—190° (decomp.), and a yellow *methiodide*, m.p. 195°. It is reduced (H_2 at 80—90°/115 atm.; Ni in EtOAc–EtOH–H_2O) but not by Na and EtOH to *α-phenyl-ββ-di*-pp′-*tetramethyldiaminodiphenylethane* (VIII), m.p. 131·5—132·5° [colourless *perchlorate*, m.p. 207—211° (decomp.); yellow *picrate*, m.p. 186°; pale yellow *methiodide*, m.p. 212°], also obtained in very poor yield from $CH_2Ph{\cdot}CHO$, NPhMe$_2$, and $ZnCl_2$ in boiling PhMe. (VIII) gives a green-blue or violet colour when oxidised by PbO_2 or chloranil respectively. $OH{\cdot}CH(C_6H_4{\cdot}NMe_2)_2$ (IX) and (II) in boiling AcOH afford *αα*-di-*pp′*-tetramethyldiaminodiphenyl-β-2-quinolylethane, m.p. 130—132° (colourless *triperchlorate*; brown-red *formate*, m.p. 57—58°; colourless *methiodide*, m.p. 153—155°), oxidised by PbO_2 to a dark red solution; it is hydrogenated to (VI). (IX) and phenylmethylpyrazolone in AcOH at 100° afford *tetramethyldiaminodiphenylphenylmethylpyrazolylmethane*, m.p. 185—195° (much decomp.), oxidised to a blue solution by PbO_2 and to a violet-red solution by chloranil. H. W.

Derivatives of 10-chlorobenz(*g*)quinoline [8-chloro-6 : 7-benzquinoline]. F. H. Gerhardt and C. S. Hamilton (*J. Amer. Chem. Soc.*, 1944, **66**, 479—480).—β-$C_{10}H_7{\cdot}NHAc$ and Cl_2 give 1 : 2-$C_{10}H_6Cl{\cdot}NHAc$ (I), which with HNO_3 (*d* 1·49) at −10° gives 1-*chloro*-5- (II), m.p. 183—185°, and -8-*nitro*-2-*acetnaphthalide* (III), m.p. 188—190°, but in AcOH at room temp. some 1-*chloro*-6-*nitro*-2-*acetnaphthalide* (IV), m.p. 221—223°, is formed. (II) (80%), (III) (65%), and (IV) (76%) are also prepared by chlorinating the appropriate $NO_2{\cdot}C_{10}H_6{\cdot}NHAc$. With glycerol, H_2SO_4, and As_2O_5, (I) gives 8-chloro-6 : 7-benzquinoline [10-chlorobenz(*g*)quinoline] (V) (34%), m.p. 138—140°, which with HNO_3 (*d* 1·49) at −18° gives 10-*chloro*-6-*nitro*- (VI) (45%), m.p. 211—212°, and -9-*nitro*-*benz*(g)*quinoline* (VII) (12%), m.p. 209—211°. With glycerol and As_2O_5 in 70% H_2SO_4 at the b.p., (II), (III), and (IV) give (VI), (VII), and 10-*chloro*-7-*nitrobenz*(g)*quinoline* (VIII) (4%), m.p. 243—245°, respectively. With morpholine and a little KI or with piperidine, (V) at 150° yields 10-*morpholino*- (6%), m.p. 160—161°, and 10-*piperidino*-*benz*(g)*quinoline* (8%), m.p. 97—99°, respectively. Morpholine and a trace of Cu-bronze convert (VI) and (VIII) at the b.p. into 6- (5%), m.p. 156—158°, and 7-*nitro*-10-*morpholinobenz*(g)*quinoline* (3%), m.p. 202—204°. $NHEt_2$ does not react with (V), (VI), or (VIII). Passing Cl_2 into (V) in $CHCl_3$ gives 5 : 10-dichlorobenz(*g*)quinoline (71%), m.p. 213—215° (cf. *loc. cit.*), the structure of which is proved by oxidation (CrO_3–AcOH) to benz(*g*)quinoline-5 : 10-dione [1-aza-anthraquinone], m.p. 278—280°. With CrO_3–AcOH at the b.p. (VI) gives 6-*nitrobenz*(g)*quinoline*-5 : 10-*dione* [6-*nitro*-1-*aza*-*anthraquinone*] (42%), m.p. 243—245°, and with boiling Fe–AcOH–H_2O gives 10-*chloro*-6-*aminobenz*(g)*quinoline* (30%), m.p. 181—183°



(V.)

R. S. C.

Derivatives of 1 : 10-phenanthroline. F. Richter and G. F. Smith (*J. Amer. Chem. Soc.*, 1944, **66**, 396—398).—Yields in Skraup reactions (As_2O_5–H_2SO_4; 130—135°) quoted below are dependent on optimum conditions which are defined. 2 : 4 : 1-$NO_2{\cdot}C_6H_3Cl{\cdot}NH_2$ (43·1 g.) gives 6-chloro-8-nitro- (47—48 g.), m.p. 159°, and thence 6-chloro-8-amino-quinoline, m.p. 73°, and 5-chloro-1 : 10-phenanthroline (56%), m.p. 123° (cf. Kuczynski *et al.*, A., 1937, II, 116). 2 : 4 : 1-$NO_2{\cdot}C_6H_3Br{\cdot}NH_2$ (54·3 g.) gives 6-bromo-8-nitro- (60 g.), m.p. 170°, and thence 6-bromo-8-amino-quinoline, m.p. 78°, and 5-*bromo*-1 : 10-*phenanthroline* (I) (46%), m.p. (+H_2O) 86° or (anhyd.) 119°. The so-called (I) (m.p. 215°) of F.P. 804,454 must have a different structure. 4 : 2 : 1-$NO_2{\cdot}C_6H_3Mc{\cdot}NH_2$ (38 g.) gives 8-nitro- (38—40 g.), m.p. 121—122°, and thence 8-amino-6-methylquinoline, m.p. 73°, and 5-*methyl*-1 : 10-*phenanthroline* (II) (66%), m.p. 114°, b.p. 280—282°/13 mm. (*picrate*, m.p. 203—204°). The Me of (II) facilitates nitration (HNO_3–H_2SO_4; 120°), which yields a 5-NO_2-compound, m.p. 268—270°. R. S. C.

Syntheses in the carbazine series. H. Goldstein and G. Huser (*Helv. Chim. Acta*, 1944, **27**, 616—619; cf. A., 1928, 647).—*o*-$C_6H_4Me{\cdot}NH{\cdot}C_6H_4{\cdot}CO_2H$-*p* is converted by MeOH–conc. H_2SO_4 into the *Me* ester, m.p. 48·5°, which with MgPhBr in Et_2O yields 2-p-*tolylaminotriphenylcarbinol*, m.p. 164·5°; this is dehydrated by glacial AcOH containing HCl to 5 : 5 *diphenyl*-3-*methyl*-5 : 10-*dihydroacridine*, m.p. 217°. Similarly *Me* N-p-*anisylanthranilate*, m.p. 53·5°, yields successively 2-p-*anisidinotriphenylcarbinol*, m.p. 123°, and 3-*methoxy*-5 : 5-*diphenyl*-5 : 10-*dihydroacridine*, m.p. 213—214°. *Me* N-β-*naphthylanthranilate*, m.p. 53°, is converted into 2-β-*naphthylaminotriphenylcarbinol*, m.p. 132—133°, and thence into 5 : 5-*diphenyl*-5 : 10-*dihydro*-3 : 4-*benzacridine*, m.p. 260—261°. M.p. are corr. H. W.

Thiobarbituric acids.—See B., 1944, III, 119.

Pyrrole series. XI. Effect of substituents on the structure of dipyrrylmethenes. Relationships between dipyrryl- and triphenylmethane dyes. K. J. Brunings and A. H. Corwin (*J. Amer. Chem. Soc.*, 1944, **66**, 337—342; cf. A., 1943, II, 72).—By electronic influences passage of dipyrrylmethyl bromides (*A*) into dipyrrylmethene anhydro-bases or hydrobromides is favoured by substitution of the pyrryl by Me and hindered by substitution by CO_2Et. By preventing planar alignment (and thus resonance), 5-CO_2Et is much more effective than 3- or 4-CO.Et, and 1-Me hinders the transformation. In extreme cases (*A*) exist as such and yield carbinols and carbinol ethers, but are converted into methene stannichlorides by $SnCl_4$; in less extreme cases (*A*) do not exist as such but with KOH–EtOH give the carbinol ether, though aq. KOH may give the carbinol or methene anhydro-base. (*A*) thus resemble triphenylmethyl halides; in the latter series steric reasons as above account for the lack of effect of *o*-substituents. Et_2 3 : 5 : 3′ : 5′-tetramethyldipyrrylmethene-4 : 4′-dicarboxylate hydrobromide (prep. from the methane by Br–CCl_4) with $Ca(OH)_2$ in $CHCl_3$ gives the red anhydro-base, m.p. 189—190° (decomp.). Et_2 4 : 5 : 4′ : 5′-tetramethyldipyrrylmethene-3 : 3′-dicarboxylate hydrobromide, similarly prepared, gives similarly the orange-red anhydro-base, m.p. 164—165° (decomp.). *Et*$_2$ 3 : 4 : 3′ : 4′-*tetramethyldipyrrylmethene*-5 : 5′-*dicarboxylate hydrobromide* (I) (prep. as above), decomp. 160—165°, gives no anhydro-base but with, *e.g.*, H_2O gives 5 : 5′-*dicarbethoxy*- 3 : 4 : 3′ : 4′-*tetramethyldipyrrylcarbinol*, decomp. 185—186°, and in boiling MeOH gives the *Me ether*, m.p. 169—170° (decomp.), thereof, both reconverted into (I) by HBr–CCl_4. Et_3 3 : 5 : 4′-trimethyldipyrrylmethene-4 : 3′ : 5′-tricarboxylate hydrobromide (similarly prepared) with KOH–MeOH gives the carbinol Me ether but with $Ca(OH)_2$–$CHCl_3$ gives the methene anhydro-base, m.p. 125—126° (decomp.). The appropriate methane with Br–CCl_4 gives 3 : 5 : 3′ : 5′-*tetracarbethoxy*-4 : 4′-*dimethyldipyrrylmethyl bromide*, m.p. 132—133° (decomp.), which becomes coloured in hot C_6H_6 and colourless again on cooling, colours filter-paper and textiles, becomes only weakly coloured in conc. H_2SO_4, but with $SnCl_4$ in $CHCl_3$ gives a colour (the methene stannichloride), destroyed by H_2O. The appropriate methane and Br–CCl_4 in complete absence of H_2O give 4 : 3′ : 5′-*tricarbethoxy*-1 : 3 : 5 : 1′ : 4′-*pentamethyldipyrrylmethyl bromide*, m.p. 135—136° (red), which gives brilliant colours in conc. H_2SO_4 or $HClO_4$ or with $SnCl_4$–$CHCl_3$, and in boiling MeOH gives the *carbinol Me ether*, m.p. 93—94°. R. S. C.

Molecular rearrangements of phenyl styryl ketone oxides.—See A., 1944, II, 224.

Some basically substituted derivatives of benziminazole and lupinane. G. R. Clemo and G. A. Swan (*J.C.S.*, 1944, 274—276).—4-Nitro-3-(ε-diethylamino-β-amyl)aminoanisole, prepared from 3-bromo-4-nitroanisole, is identical with the product obtained from 3 : 4-dinitroanisole (cf. Toptschiev, A., 1936, 838). 4-Bromo-3-nitroanisole with δ-amino-α-diethylaminopentane and Cu (trace) give 3-*nitro*-4-(ε-*diethylamino*-β-*amyl*)*aminoanisole*, b.p. 195—200°/2 mm., reduced ($SnCl_2$–HCl) to the 3-NH_2-compound (I), b.p. 180—185°/2 mm. 4-Amino-3-(ε-diethylamino-β-amyl)aminoanisole (II)

with HCO_2H affords 1-(ε-*diethylamino-β-amyl*)-6-*methoxy-benziminazole*, b.p. 190°/1·5 mm. (*dipicrolonate*, m.p. 193°), and with Ac_2O yields the -2-*methylbenziminazole*, b.p. 190°/1·5 mm. (*dipicrolonate*, m.p. 230°). Similarly, (I) with HCO_2H gives 5-*methoxy*-1-(ε-*diethylamino-β-amyl*)*benziminazole*, b.p. 195°/2 mm. (*picrate*, m.p. 161°), and with Ac_2O forms the 2-*Me* derivative, b.p. 195°/2 mm. (*dipicrate*, m.p. 198°). 11-Bromolupinane condenses similarly to give 11-(ε-*diethylamino-β-amyl*)*aminolupinane*, b.p. 165—167°/2 mm. (*tripicrolonate*, m.p. is 166—172°). Condensation of (II) with CH_2Ac_2 affords a *base*, $C_{21}H_{28}O_2N_2$, b.p. 175°/1·5 mm. F. R. S.

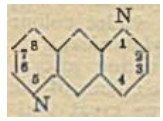
Reaction between aromatic diamines and dicarboxylic acids. I. *o*-Phenylenediamine and phthalic anhydride. B. A. Porai-Koschitz and M. M. Antoschulskaja (*J. Gen. Chem. Russ.*, 1943, **13**, 339—352). —*o*-$C_6H_4(NH_2)_2$ (I) and *o*-$C_6H_4(CO)_2O$ (II) (1 : 1 mol.) at 120—130° (oil-bath) gave 70% of benzoylenebenziminazole (III), m.p. 209·5—210° (extracted from the cooled melt with Ac_2O), diphthaloyl-*o*-phenylenediamine (IV), and *o*-di-2-benziminazolylbenzene (V); (IV) and (V) are insol. in Ac_2O and were separated by treatment with dil. HCl, crystallisation, and distillation. The use of C_5H_5N for the extraction and crystallisation of (III) leads to an impure product, indicating the presence in the melt of *o*-2-benziminazolylbenzoic acid, which is converted into (III) by Ac_2O. (IV), m.p. 296·5—297°, and diphthaloyl derivatives of other diamines are best prepared by slowly adding (I) to 7 mols. of boiling (II); the cooled melt is extracted with boiling 20% aq. Na_2CO_3, washed with H_2O, extracted with hot EtOH to remove (III), and cryst. from glacial AcOH. (V), m.p. 414—416°, was prepared in 70% yield by fusing together (I) and (II) (4 : 1 mol.) at 185—190° (oil-bath), extracting the melt with boiling aq. Na_2CO_3 and then with boiling dil. HCl; slow crystallisation of the acid extract and decomp. of the HCl salt, or direct neutralisation of the acid extract with NH_3, gave the base, which was purified by extraction with boiling polychlorobenzene, b.p. 183—187°, followed by C_6H_6, and final sublimation. Fusion of (III) with excess of (I) at 195° gave (V) in 92·6% yield; of (IV) with (I) (1 : 1 mol.) at 230—240° gave 30·9% of (III) together with (V); of (IV) with excess of (I) at 240—250° gave (V) in 89% yield. (III) with excess of (II) at 195° did not react, but addition of (III) to excess of boiling (II) gave 10% of (IV); (V) did not react with (II) under similar conditions, nor in the presence of C_5H_5N or piperidine. R. C. P.

***N*⁴-Substituted sulphonamides.** J. Finkelstein (*J. Amer. Chem. Soc.*, 1944, **66**, 407—408).—The appropriate sulphanilamido-compound and $CH_2Cl{\cdot}COCl$ in C_5H_5N give *p*-$CH_2Cl{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$, m.p. 211—213°, 2-*N*⁴-*chloroacetylsulphanilamido-pyridine*, m.p. 192—193°, *-thiazole*, m.p. 205—206°, *-4-methylthiazole*, m.p. 231—232°, and *-pyrimidine*, m.p. 208—210°, converted by conc. aq. NH_3 at 40° into the *glycyl* derivatives, m.p. (I) 216—218°, 220—221°, 215—216°, 205—206°, and 238—240°, respectively. The substance, m.p. 260°, of Pollak *et al.* (A., 1931, 1283, m.p. 256—258°), supposed to be (I), is *iminobis*-*N*⁴-*acetylsulphanilamide*. 2-*N*⁴-Hexoylsulphanilamido-pyridine, m.p. 193—194°, -thiazole, m.p. 193—195°, and *-pyrimidine*, m.p. 214—215°, are also prepared. The drugs have low toxicity and may be useful therapeutically (preliminary data only are given). R. S. C.

Heterocyclic compounds containing nitrogen. LII. Pyridylisatogens. P. Ruggli and H. Cuenin (*Helv. Chim. Acta*, 1944, **27**, 649—662).—2-Methylpyridine, *o*-$NO_2{\cdot}C_6H_4{\cdot}CHO$, and Ac_2O at 170—175° give 2-nitrostilbazole, m.p. 100—101° [hydrochloride, m.p. 213—215° (decomp)]; the dibromide, m.p. 181° (*picrate*, m.p. 174°), loses Br when treated with C_5H_5N, piperidine, KOH–EtOH, AgOAc, or AgOBz. The corresponding *dichloride*, m.p. 143·5—144° [*hydrochloride*, m.p. 176° (decomp.); *picrate*, m.p. 167—168° (decomp.)], is converted by prolonged boiling with C_5H_5N into *μ-chloro-2-nitrostilbazole*, m.p. 61·5—62° [*hydrochloride*, m.p. 160—165° (decomp.); *picrate*, m.p. 128—128·5°], and by boiling KOH–MeOH into 2-nitrotolazole (I), m.p. 54·5—55°, [picrate, m.p. 171—171·5°; *hydrochloride*, m.p. 158°, resinifies when kept; very hygroscopic *sulphate*, m.p. 73—76°; *dibromide hydrobromide*, m.p. 250—252° (decomp.)]. (I) is transformed into 2-2′-*pyridylisatogen* (II), m.p. 182° [also +1$CHCl_3$; *picrate*, m.p. ~177° (decomp.); *hydrochloride*, m.p. 195—196°; *sulphate*, m.p. 215° (decomp.); *oxalate*, m.p. 160°; *methiodide*, m.p. 182°; additive *compound*, m.p. 119—120°, with H_2SO_3], slowly by insolation in C_5H_5N, rapidly by PhNO (functioning at " stoicheiometric catalyst "). (II) and NH_2OH,HCl in boiling EtOH afford the C-*oxime*, m.p. 215—217° (decomp.), reduced by Zn dust in boiling AcOH to which Ac_2O is subsequently added to 3-*acetamido*-2-*pyridylindole* (III), m.p. 189°, or, if addition of Ac_2O is omitted, to 3-*amino*-2-*pyridylindole*, m.p. 240°, softens at 100° and blackens at ~170°. (II) and NHPh·NH_2 in EtOH at >40° evolve N_2 and give 1 : 3-*dihydroxy*-2-2′-*pyridylindole* (*indolone hydrate*) (IV), m.p. 163—165° (decomp.), softens >140° (*hydrochloride*), with a small proportion of 2-2′-*pyridylindolone* (V), m.p. 186° [*picrate*, m.p. 202° (decomp.)], which is the main product from (II) and NHPh·NH_2 in boiling EtOH; the *oxime*, m.p. 179—180° (blackens), is reduced by Zn dust and AcOH followed by Ac_2O to (III). (II) is reduced (Zn dust–AcOH–Ac_2O or catalytically in presence of Raney Ni and Ac_2O) to 3-*acetyl*-2-*pyridylindoxyl* (VI), m.p. 129·5—130·5°, also obtained from (IV) and (V). In absence of Ac_2O (II) affords *indoloneindoxyl*, $C_6H_4\langle CO \atop NH \rangle CR{\cdot}O{\cdot}C\langle C_6H_4 \atop CR \rangle NH$ (R = C_5H_4N), decomp. (indef.) 210—230° [*picrate*, m.p. 205—207° (decomp.)], also obtained by reduction of (II) with KI–HCl. (II), (IV), or (V) yields with piperidine in boiling EtOH an *adduct*, $C_{18}H_{19}ON_3$, m.p. 184—185°; when treated with NaOH it gives piperidine, with 2N-HCl at 40° it gives (IV), and in cold dioxan it slowly yields (V) and a red resin. It is reduced (Zn dust–AcOH–Ac_2O) to (VI). (II) is transformed by H_2SO_4–EtOH at 100° into (?) 2-*pyridylisoisatogen*, m.p. 105—107°. H. W.

Hydrogenation-dehydrogenation reactions involving compounds of ammono-aldehyde, ammono-acetal, and aquo-ammono-aldehyde types. P. J. McLaughlin and E. C. Wagner (*J. Amer. Chem. Soc.*, 1944, **66**, 251—254).—The mechanism proposed by Simons (A., 1937, II, 185) for the conversion of $CH_2(NH{\cdot}C_6H_4Me\text{-}p)_2$ (I) into the dihydroquinazoline (II) is confirmed and extended. Conversion of the intermediate tetrahydroquinazoline (III) into (II) is a crossed Cannizzaro reaction in which (I) or the trimer of *p*-$C_6H_4Me{\cdot}N{:}CH_2$ (IV) functions as proton-acceptor; this function is exercised by dissociation into (IV) or, in acid at a lower temp., the cation thereof. The reaction is shown to be irreversible and independent of H_2O, air, or picric acid (used as precipitant). The proton-acceptor may also be CHPh:NPh, methylenebispiperidine, NPh:CH·NHPh, *p*-$C_6H_4Me{\cdot}NH{\cdot}CHO$, or $HCO{\cdot}NH_2$ (*i.e.*, substances of aldehydic or ammono-aldehydic type), but not NPh:CMe·NHPh, NHPhAc, or NH_2Ac. Sources of acid may be, in order of decreasing efficiency, *p*-$C_6H_4Me{\cdot}NH_2$,HCl, NMe_3,HCl, the hydrochloride of (II), piperidine hydrochloride, or NH_4Cl, which, except for NH_4Cl, accords with their activities as proton donors. R. S. C.

Heterocyclic compounds containing nitrogen. LI. New linear benzodipicoline, 2 : 6-dimethyl-1 : 5-anthrazoline. P. Ruggli and F. Brandt (*Helv. Chim. Acta*, 1944, **27**, 274—291; cf. A., 1938, II, 460).—Derivatives of 2 : 6-dimethyl-1 : 5-anthrazolone (cf. *A*) are described. 1 : 4 : 2 : 5-$C_6H_2Me_2Cl_2$ (*I*) (prep. from *p*-xylene and Cl_2 in presence of Fe powder and absence of light described) is converted by dry Cl_2 in strongly irradiated $C_6H_3Cl_4$ at 120—130° into 2 : 5 : 1 : 4-$C_6H_2Cl_2(CHCl_2)_2$, b.p. 313°, m.p. 72·5—74°, converted by NH_2Ph at 100° into the *tetraanilino*-compound, darkens >260°, and hydrolysed by conc. H_2SO_4 at 170° to 2 : 5 : 1 : 4-$C_6H_2Cl_2(CHO)_2$ (II), m.p. 157—158° (*dianil*, m.p. 213—214°). Chlorination of (I) at 130—140° in light in absence of solvent or catalyst affords 1 : 4 : 2 : 3 : 5 : 6-$C_6Me_2Cl_4$, m.p. 217·5°, and in strongly illuminated, technical $C_6H_3Cl_3$ at 120—130° gives 2 : 3 : 5 : 6-*tetrachloro*-1 : 4-*dichloromethylbenzene*, m.p. 174·5—175° (*dianilino*-compound, m.p. 170°). 2 : 5-*Dichloro*-1 : 4-*di*(*trichloromethyl*)*benzene*, m.p. 193°, is obtained by chlorinating (I) in illuminated C_2HCl_3 at 130—145°. Gradual addition of Br to (I) at 120—180° and finally at 210° yields 2 : 5 : 1 : 4-$C_6H_2Cl_2(CHBr_2)_2$, hydrolysed to (II). Gradual addition of Br to illuminated 1 : 4 : 2 : 5-$C_6H_2Me_2Br_2$ (prep. from *p*-xylene described) containing I at 120° and finally at 170° gives 2 : 5-*dibromo*-1 : 4-*di*(*dibromomethyl*)*benzene*, m.p. 162—163°, hydrolysed by H_2SO_4,H_2O at 130—140°/25 mm. to 2 : 5-*dibromoterephthalaldehyde* (III), m.p. 189—190·5° (corresponding *dianil*, m.p. 234·5—235°). (III) is converted by NH_2Ac at 135—140° into 2 : 5-*dibromoterephthalletra-acetamide*, darkens at 305° and carbonises at a higher temp., and by *p*-$C_6H_4Me{\cdot}SO_2{\cdot}NH_2$, Cu powder, CuBr, and K_2CO_3 in $PhNO_2$ according to conditions into *o-bromo*-2-p-*toluenesulphonamido*-, m.p. 183—185°, or 2 : 5-*di*-p-*toluenesulphonamido*- (IV) *-terephthalaldehyde*, m.p. 241—243° (decomp.) [*dipiperidine* salt, decomp. 140°, reddens at 110°; *dianil*, m.p. 297° (decomp.)]. (IV) is transformed by $CH_2Ac{\cdot}CO_2Et$ in presence of piperidine at 70° into Et_2 2 : 5-*di*-p-*toluenesulphonamidoterephthalylidenediacetoacetate* (V), m.p. 216—217° (decomp.), becomes discoloured at 210°, which with NH_2Ph at 100° affords a *compound*, $C_{54}H_{48}O_6N_6S_2$, m.p. 299—301° (decomp.). (V) with conc. H_2SO_4 at 27—32° suffers one-sided ring-closure to *Et* 6-*amino*-3-*carbethoxy*-2-*methylquinoline*-7-*methenylacetoacetate* (VI), m.p. 219—220° (*picrate*, decomp. 215—220°, softens at 200°), hydrolysed to the dicarboxylic *acid* (VII), decomp. >280° (*Na*₂ salt). Under more drastic conditions conc. H_2SO_4 causes two-sided ring-closure of (V) to 2 : 6-*dimethyl*-1 : 5-*anthrazoline*-3 : 7-*dicarboxylic acid* (2 : 6-*dimethyl*-lin-p-*benzodipyridine*-3 : 7-*dicarboxylic acid*), decomp. ~320°, becomes brown at 280°, also obtained from (VI) and (VII). This is decarboxylated by Cu powder and Cu chromite in quinoline at 215° to 2 : 6-*dimethyl*-1 : 5-*anthrazoline*, needles, m.p. 238—239° (decomp.), or apparently hydrated leaflets, which give solutions in dil. HCl or H_2SO_4 from which it is repptd. by Na_2CO_3 but not by NaOAc. It gives a cryst. oxalate, perchlorate, chromate, and *picrate*, decomp. ~263°, becomes discoloured at 250°, a (*CHPh:*)₂, m.p. 267°, and a *di*-p-*dimethylaminobenzylidene*, decomp. 340°, derivative. (IV) is transformed by COPhMe at 190—197° into 2 ; 6-*dibhenyl*-1 ; 5-*anthrazoline*, m.p. 284—285° (*picrate*, m.p. 283°). H. W.



(*A.*)

Tetrahydrotriazines.—See B., 1944, II, 158.

Morpholinomethylurea.—See B., 1944, II, 157.

αβ-Diamino-ketones. II. Reactions of thalline and open-chain *sec.* amines with α-bromo-β-amino-ketones. N. H. Cromwell, J. A. Caughlan, and G. F. Gilbert (*J. Amer. Chem. Soc.*, 1944, **66**, 401—403; cf. A., 1944, II, 171).—Interaction of α-bromo-β-heterocyclic amino-β-phenylpropiophenone (or the COMe compound) with open-chain *sec.* bases gives poor yields of mixed diamino-ketones, mainly owing to steric reasons. *p*-OMe·C_6H_4·NH_2, $FeSO_4$, *p*-OMe·C_6H_4·NO_2, glycerol, and H_2SO_4 at the b.p. give 6-methoxyquinoline (53%), m.p. 18—20°, b.p. 182—184°/34 mm., which with H_2–Cu chromite in EtOH at 180°/1800 lb. gives 6-methoxy-1 : 2 : 3 : 4-tetrahydroquinoline (93%), m.p. 42—43°, b.p. 127—130°/1 mm. (picrate, m.p. 164—165°). α-Bromo-β-piperidino-β-phenylpropiophenone (I) with the appropriate amine in EtOH at 70° gives *α-piperidino-β-6-methoxy*-1 : 2 : 3 : 4-*tetrahydroquinolino-β-phenylpropiophenone* (85%), m.p. 159—160°; similarly are prepared *α-morpholino-β-6-methoxy*-1 : 2 : 3 : 4-*tetrahydroquinolinopropiophenone* (68%), m.p. 143°, *α-piperidino-* (39%), m.p. 124°, and *α-morpholino-β-6-methoxy*-1 : 2 : 3 : 4-*tetrahydroquinolino-β-phenylethyl Me ketone* (40%), m.p. 126°. CH_2Ph·NHMe and (I) in 1 : 3 EtOH–Et_2O at room temp. (12 hr.) and then 0° (2 days) give *β-N-methylbenzylamino-α-piperidino-β-phenylpropiophenone* (36%), m.p. 138—140°, hydrolysed by 15% H_2SO_4 at 100° to ω-piperidinoacetophenone; similarly are prepared *α-piperidino-β-N-methyl-N-β′-hydroxyethylamino-β-phenylpropiophenone* (10%), m.p. 108°, *α-piperidino-β-N-methylbenzylamino-* (14%), m.p. 111°, and *-β-N-methyl-N-β′-hydroxyethylamino-β-phenylethyl Me ketone* (5%), m.p. 132°. NH(CH_2Ph)$_2$ with (I) at room temp. and then 0° gives *α-piperidino-β-dibenzylamino-β-phenylpropiophenone* (13%), m.p. 173—175° (decomp.), and with α-bromo-β-piperidino-β-phenylethyl Me ketone in 37 : 63 EtOH–Et_2O at room temp. and then 0° gives *α-piperidino-β-dibenzylamino-β-phenylethyl Me ketone* (4%), m.p. 158—160° (decomp.). R. S. C.

Further 2-*p*-nitrophenyl-4-alkyloxazol-5-ones. P. Karrer and C. Christoffel (*Helv. Chim. Acta*, 1944, **27**, 622—623; cf. A., 1943, II, 187).—*dl*-Phenylalanine in 2N-NaOH is converted by *p*-NO_2·C_6H_4·COCl in Et_2O into 2-p-*nitrophenyl-4-benzyloxazol-5-one*, m.p. 162°, which with NaOH–Et_2OH gives a dark violet colour becoming blue on addition of C_5H_5N; N-p-*nitrobenzoylalanine*, m.p. 168·5°, is obtained as by-product. Similarly, *dl*-valine affords 2-p-*nitrophenyl*-4-iso*propyloxazol-5-one*, m.p. 92°. The colour of the alkali salts of the oxazolones in different media shows great variations which do not appear related to the dielectric const. of the liquids. H. W.

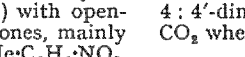
Chemotherapy of bacterial infections. IX. Synthesis of some sulphathiazole derivatives. K. Ganapathi. **X. 2-Acetsulphanilimido-3-acetsulphanilylthiazolone and 2-diacetsulphanilylamidothiazole. New route to sulphathiazole.** C. V. Deliwala, K. Ganapathi, and M. V. Shirsat (*Proc. Indian Acad. Sci.*, 1943, **18, A**, 355—359, 360—363).—IX. The Na salt of sulphathiazole condenses with the appropriate alkyl bromide or iodide in EtOH to give 2-(p-*aminobenzenesulphonimido*)-3-*methyl-*, m.p. 244—246°, *-ethyl-*, m.p. 183—185°, -n-*butyl-*, m.p. 186—188°, -iso*amyl-*, m.p. 201—203°, -n-*hexyl-*, m.p. 156°, *-β-hydroxyethyl-*, m.p. 154—156°, *-β-ethoxyethyl-*, m.p. 150—152°, *-acetonyl-*, m.p. 202°, and *-carboxymethylthiazolone*, m.p. 184—185°. Of these compounds only the Me derivative shows good therapeutic activity.

X. 2-Aminothiazole condenses with acetylsulphanilyl chloride in H_2O or suspension in presence of $NaHCO_3$, $CaCO_3$, or $BaCO_3$ to yield 2-diacetsulphanilylamidothiazole, m.p. 128—129°, which in boiling EtOH isomerises to 2-acetsulphanilimido-3-sulphanilylthiazolone. These two products are hydrolysed by acid or alkali to sulphathiazole in good yield. F. R. S.

Synthesis of the aluminium and the magnesium salts of thiolbenzthiazole. K. D. Petrov and A. M. Fedortschenkova (*J. Appl. Chem. Russ.*, 1943, **16**, 211—213).—The *salt*, Al(OH)$(C_7H_4NS_2)_2$,H_2O, from $Al_2(SO_4)_3$ and a saturated solution of thiolbenzthiazole (I) in NaOH, is easily hydrolysed. The *salt*, $Mg(C_7H_4NS_2)_2$, is prepared from (I) and MgO at 160—170°. J. J. B.

Preparation of the zinc salt of thiolbenzthiazole and its transformation during vulcanisation of rubber. K. D. Petrov (*J. Appl. Chem. Russ.*, 1943, **16**, 214—218).—A saturated solution of thiolbenzthiazole (I) in 1% NaOH with a 2·5% solution of $Zn(OAc)_2$ yields the *salt*, $Zn(C_7H_4NS_2)_2$ (II), which with 0·05 part of S in boiling xylene gives ZnS, (I), and a little dibenzthiazolyl disulphide (III), and with H_2S in C_6H_6 gives ZnS and (I). From rubber vulcanised by means of (II) and S, COMe$_2$ extracts (I). Probably, during vulcanisation (II) reacts with S, giving (III), which with H_2S forms (I) and active S, causing vulcanisation. J. J. B.

Synthesis and constitution of vitachrome. P. Karrer and M. C. Sanz (*Helv. Chim. Acta*, 1944, **27**, 619—621).—$(CS·NH_2)_2$ and COMe·CHCl·$[CH_2]_2$·OH at 120° afford 4 : 4′-dimethyl-5 : 5′-di-β-hydroxyethyl-2 : 2′-dithiazolyl (vitachrome) (I), m.p. 180°, which when pure forms completely colourless needles with pure blue fluorescence in ultra-violet light. Its formation by irradiation of 2-chloro-4-methyl-5-β-hydroxyethylthiazole is due to dissociation of this compound into Cl atoms and residual radicals which become dimerised. Similarly COMe·CHCl·$[CH_2]_2$·OAc affords vitachrome diacetate, m.p. 116—116·5°. The destruction of the fluorescence of (I) by aq. $Na_2S_2O_4$ (restored by shaking with air) is not due to the formation of a non-fluorescent reduction product since Na_2 4 : 4′-dimethyl-2 : 2′-dithiazolyl-5 : 5′-dicarboxylate does not evolve CO_2 when treated with $Na_2S_2O_4$. H. W.

Structure-chemical investigations. X. Reactive behaviour of dithioamides of aliphatic dicarboxylic acids. H. Lehr and H. Erlenmeyer (*Helv. Chim. Acta*, 1944, **27**, 489—493).—$(CS·NH_2)_2$ and $(CH_2·NH_2)_2$,H_2O (1 : 2) in boiling EtOH yield 2-*β-aminoethylaminothioformyl-iminazoline* [*-glyoxalidine*], decomp. 250—255° (*picrate*, m.p. 284—285°), readily transformed by an excess of $(CH_2·NH_2)_2$,H_2O into di-2-Δ²-iminazolinyl,  m.p. 290—298° (cf. Forssel, A., 1891, 1003). Adipdithioamide (I) and $(CH_2·NH_2)_2$,H_2O in EtOH or in absence of solvent afford αδ-di-2-Δ²-iminazolinylbutane, m.p. 209—210° (*picrate*, m.p. 207°); the monomeric character of the products is remarkable. (I) and $(CO·CH_2Br)_2$ in abs. EtOH at room temp. give the chain *polymer*, $(C_{10}H_{10}N_2S_2)_n$, softens at 230° and then decomposes gradually. (I) and CH_2BzBr readily yield *αδ-di-4-phenyl-2-thiazolylbutane*, m.p. 89° (*hydrobromide*, m.p. 288°). CH_2BzBr and $(CS·NH_2)_2$ yield 4 : 4′-*diphenyl*-2 : 2′-*dithiazolyl*, m.p. 222°, from which a picrate or hydrobromide could not be obtained. H. W.

2 : 2′-Dithiazolyl compounds. P. Karrer, P. Leiser, and W. Graf (*Helv. Chim. Acta*, 1944, **27**, 624—625).—$(CS·NH_2)_2$ and COMe·CH_2Cl in boiling EtOH afford 4 : 4′-*dimethyl*-2 : 2′-*dithiazolyl*, m.p. 136°. Similarly $(CS·NH_2)_2$ and CHAcCl·CO_2Et at 120° give *Et*$_2$ 4 : 4′-*dimethyl*-2 : 2′-*dithiazolyl*-5 : 5′-*dicarboxylate*, m.p. 186°, hydrolysed to the *acid*, decomp. >310°. $(CS·NH_2)_2$ and $(CO·CH_2Br)_2$ in EtOH yield a polythiazole compound of high mol. wt. The compounds resemble vitachrome in giving a very pronounced fluorescence in ultra-violet light; in conc. H_2SO_4 the fluorescence is intense in daylight. H. W.

Cyanine type dyes.—See B., 1944, II, 160.

VII.—ALKALOIDS.

Synthesis of *dl*-heliotridane (1-methylpyrrolizidine). V. Prelog and E. Zalán (*Helv. Chim. Acta*, 1944, **27**, 531—534).—Addition of OPh·$[CH_2]_2$·CHMe·CN (I) to Mg γ-ethoxypropyl bromide in Et_2O leads to *α-phenoxy-η-ethoxy-γ-methylheptan-δ-one*, b.p. 100—110°/0·2 mm., the *oxime*, b.p. 150°/0·1 mm., of which is reduced by Na and abs. EtOH to *δ-amino-α-phenoxy-η-ethoxy-γ-methylheptane*, b.p. 190—191°/12 mm. The hydrobromide is transformed by 66% HBr at 100° into αη-dibromo-δ-amino-γ-methylheptane hydrobromide, which with dil. aq. NaOH affords dl-1-*methylpyrrolizidine* (dl-*heliotridane*) [*picrate*, m.p. 234—236°; *styphnate*, m.p. 196—197°; *picrolonate*, m.p. 162—163°; *aurichloride*, m.p. 200—201° (decomp.)]. The salts resemble closely those of the natural *l*-heliotridane. Only one of the two possible racemates appears to be produced. OMe·$[CH_2]_2$·Br, $CHMe(CO_2Et)_2$, and NaOEt–EtOH yield Et_2 methyl-β-methoxyethylmalonate, b.p. 111—126°/11 mm., hydrolysed and decarboxylated to *γ-methoxy-α-methylbutyric acid* (II), b.p. 114—120°/11 mm., which is less suitable than (I) as initial material for the above synthesis. (II) is converted ($SOCl_2$) through the chloride into the *amide*, m.p. 45—47°, and *anilide*, m.p. 102—103°. H. W.

Alkaloids. I. Oxidation of papaverine to papaveraldine (xanthaline) by selenium dioxide. K. N. Menon (*Proc. Indian Acad. Sci.*, 1944, **19, A**, 21—22).—This oxidation is readily effected by SeO_2 in AcOH at 100°. R. S. C.

Isolation of lupinine from technical anabasine sulphate. A. Sadikov and G. Lazurevski (*J. Gen. Chem. Russ.*, 1943, **13**, 319—321).—Anabasine (I) and lupinine (II) in the fraction of b.p. 136—139°/12 mm., obtained by Orekhov's method (A., 1931, 498; 1932, 405) from *Anabasis aphylla*, were separated by stirring and heating the mixture, dissolved in PhMe or light petroleum, with Na. When reaction was complete (1½—2 hr.), the mixture was cooled and the yellow Na lupinate filtered off and washed with PhMe or light petroleum. This may be used directly for synthesis or decomp. with H_2O to regenerate (II) (yield 97%). The mother-liquor after distillation yields (I). Light petroleum gave better results than PhMe. R. C. P.

Alkaloids of *Ammothamnus lehmanni*, Bge. A. Sadikov and G. Lazurevski (*J. Gen. Chem. Russ.*, 1943, **13**, 314—318).—Stems and leaves were extracted with EtOH containing 2% of NH_3. The extract, after evaporation, acidification, and removal of tar, was saturated with KOH and extracted first with Et_2O and then $CHCl_3$ (extracts *A* and *B* respectively). Evaporation of extract *A* gave 0·45% (on dry plant) of pachycarpine + sophocarpine (I). Evaporation of extract *B* and extraction of the residue with COMe$_2$ left a yellow powder (0·05%), from which was separated, by fractional pptn. from acid solution and recrystallisation from COMe$_2$, an

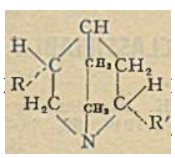
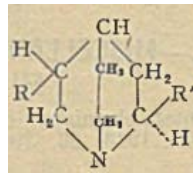
alkaloid, *ammothammine*, $C_{15}H_{24}O_3N_2$, m.p. 199—201°, $\alpha = 0°$ [*picrate*, m.p. 212—214° (decomp.); *hydriodide*, m.p. 183—189°]. The total yield of crude alkaloids from the roots was 0·12%; 0·8% of $H_2C_2O_4$ was also separated from the plant. (I) is a good insecticide. R. C. P.

Alkaloids of *Lycopodium* species. V. *L. obscurum*, L. R. H. F. Manske and L. Marion (*Canad. J. Res.*, 1944, **22**, B, 53—55).—The following have been isolated from *L. obscurum* var. *dendroideum* (Michx.) D. C. Eaton: lycopodine, obscurine, alkaloid *L*13 (cf. Marion *et al.*, A., 1944, II, 147), *alkaloid L*16, $C_{16}H_{25}ON$ (*perchlorate*, m.p. 221°), and *alkaloid L*17, $C_{18}H_{27}O_3N$ (*perchlorate*, m.p. 296°). All m.p. are corr. F. R. S.

Synthesis of possible degradation products of metathebainone. I. H. L. Holmes and L. W. Trevoy (*Canad. J. Res.*, 1944, **22**, B, 56—65).—*7-Methoxy-3 : 4-dihydro-2-naphthoic acid* (I), m.p. 149·5—150° (improved general method of prep.), is dehydrogenated (S) to *7-methoxy-2-naphthoic acid*, m.p. 195—196°, and condenses with $(CH_2{:}CH)_2$ to *3-methoxy-*, m.p. 126—127°, and with $(CH_2{:}CMe)_2$ to *3-methoxy-6 : 7-dimethyl-5 : 8 : 9 : 10 : 13 : 14-hexahydrophenanthrene-14-carboxylic acid* (II), m.p. 137·5—138·2°. The Et ester of (I) with $(CH_2{:}CMe)_2$ gives the Et ester of (II), b.p. 187°/2 mm. The acid chloride of (II) could not be converted into the corresponding aldehyde. The relationship of these hydrophenanthrenes to possible degradation products of morphine and metathebainone is discussed. M.p. are corr. F. R. S.

***Cinchona* alkaloids. VI. Configuration of (−)-γ-methyl-δ-ethylhexane.**—See A., 1944, II, 209.

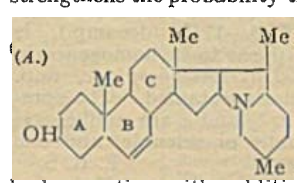
***Cinchona* alkaloids. V. Configuration of the asymmetric carbon atoms 3, 4, and 8 of the *Cinchona* alkaloids.** V. Prelog and E. Zalan (*Helv. Chim. Acta*, 1944, **27**, 535—545).—The configuration (*A*) [R = CH:CH$_2$, R′ = OMe·C_6H_5N·CH(OH)·] with the two hydrocarbon residues in the *endo* position is assigned to the dextrorotatory

(*A*.)   (*B*)

alkaloids, cinchonine and quinidine, and the structure (*B*) [R = CH:CH$_2$; R′ = C_9H_6N·CH(OH)·] to the lævorotatory cinchonidine and quinine. Cincholoipone Et ester (I), b.p. 81·5—84°/0·04 mm., 137—138°/11 mm., $[\alpha]_D^{17}$ +16·75° to 16·85°±0·05° (cf. Kaufmann *et al.*, A., 1917, i, 50), obtained by the degradation of cinchonine or by hydrogenation of meroquinine Et ester, is converted into its *hydrochloride*, m.p. 159—160°, $[\alpha]_D^{23}$ −9·3°±1° in EtOH, $[\alpha]_D$ −7·0°±1° in H_2O; the hydrochloride of the free base has m.p. 202—203°, $[\alpha]_D^{6}$ −4·6°±1° in H_2O. The ester is reduced by Na and abs. EtOH to 3-ethyl-4-β-hydroxyethylpiperidine, b.p. 103—108°/0·02 mm., $[\alpha]_D^{17}$ +13·1°±0·4° in EtOH, which with fuming HBr at 110° gives 3-ethyl-4-β-bromoethylpiperidine hydrobromide, m.p. 115—117°, $[\alpha]_D^{18}$ −16·9°±0·5° in EtOH. This is converted by Zn dust and AcOH at 80—90° into cis(+)-3 : 4-*diethylpiperidine*, b.p. 70°/12 mm., $[\alpha]_D^{22}$ +26·0±0·6° in EtOH, +37·7°±0·6° in $CHCl_3$ (*picrate*, m.p. 110·5—111°). The N-*Bz* derivative, b.p. 136°/0·2 mm., is transformed by PBr_5 into (+)-αε-*dibromo-βγ-diethylpentane* (I), b.p. 127—134°/12 mm., $[\alpha]_D^{21}$ +11·64°±0·02° in substance, $[\alpha]_D^{19}$ +11·8°±0·3° in EtOH, converted by H_2 (Raney Ni in alkaline solution) into (−)-γ-*methyl-δ-ethylhexane*, a liquid, $[\alpha]_D^{18}$ −11·70° to −12·05°±0·05° in substance, $[\alpha]_D^{17}$ −9·1°±0·6° in $CHCl_3$. The space arrangement of this methine can be transferred therefore to $C_{(3)}$ of the cinchona alkaloids. (I) is converted by $CH_2(CO_2Et)_2$ and NaOEt in EtOH at 120° into *Et*$_2$ (−)-cis-3 : 4-*diethyl*cyclo*hexane*-1 : 1-*dicarboxylate*, b.p. 116—121°/0·1 mm. The corresponding *acid*, m.p. 163—164°, $[\alpha]_D^{6}$ −11·2°±1° in $CHCl_3$, is decarboxylated at 180° to the non-cryst. cis-3 : 4-*diethyl*cyclo*hexanecarboxylic acid*, $[\alpha]_D^{16}$ −2·13°±0·05°, the Ag salt of which is converted by Br in dry, boiling CCl_4 into 1-*bromo*-cis-3 : 4-*diethyl*cyclo*hexane*, b.p. 136—156° (bath)/12 mm., $[\alpha]_D^{6}$ −1·41°±0·5° in EtOH. This is converted by H_2 (Raney Ni in EtOH containing NaOEt) into cis-1 : 2-*diethyl*cyclo*hexane*, $[\alpha]_D = 0°$. Since the two asymmetric C are not disturbed during these reactions and could not have been racemised the Et groups are in the *cis* position to one another. The *cis* relationship of the residues R and R′ at $C_{(3)}$ and $C_{(4)}$ of the products of the degradation of the cinchona alkaloids is thus established. The configuration at $C_{(8)}$ follows the observation (on models) that only compounds in which the hydrocarbon residues at $C_{(3)}$ and $C_{(8)}$ are in the *endo* relationship can give compounds with ether rings. M.p. are corr. H. W.

Partial Hofmann degradation of emetine and its dehydrogenation to emetamine. A. Ahl and T. Reichstein (*Helv. Chim. Acta*, 1944, **27**, 366—381).—The results are compatible with but do not establish the constitutional formulæ proposed for emetine (I) by Spath *et al.* (A., 1927, 471) and Brindley *et al.* (*ibid.*, 682) but cannot be reconciled with the formula of Staub (*Diss., Zurich*, 1927). (I) in Et_2O is transformed by 10% KOH and Ac_2O at room temp. into N-*acetylemetine*, m.p. 97—99° [*methiodide* (II), m.p. 213—216°; *methochloride*, m.p. 192—195°; *methoaurichloride*, m.p. 127—129°; *methoplatinichloride*, m.p. 213—217° (decomp.)]. (II) is converted by Ag_2O and solid KOH followed by cautious thermal decomp. and reacetylation into the amorphous methine *base*, $C_{32}H_{44}O_5N_2$ [*methiodide* (III), m.p. 239—240°; *methochloride*, m.p. 217—225°; *methoaurichloride*, m.p. 137—141°]. Hofmann degradation of (III) followed by reacetylation leads to a base (*methoaurichloride*, m.p. 111—118°), the *methiodide*, $C_{34}H_{49}O_5N_2I$, m.p. (indef.) 165—175°, of which is degraded under strictly defined conditions into NMe_3 and a neutral *compound* (IV), $C_{31}H_{39}O_5N$, in which the originally *tert.* N is completely absent whilst the *sec.* N remains unchanged as its Ac derivative. Oxidation of (IV) by $KMnO_4$–$COMe_2$ gives *m*-hemipinic acid (V) as sole isolable compound whereas with $KMnO_4$–dil. H_2SO_4 the products are (V) and 4 : 5-dimethoxyphthalonimide (VI), needles, m.p. 269—275° (decomp.), or occasionally granules which are converted into needles at 200°, obtained by Hermanns (*Diss., Freiberg i. Br.*, 1915) by the oxidation of (I) with CrO_3. The structure of (VI) is confirmed by its prep. by oxidation of 6 : 7-dimethoxytetrahydro*iso*quinoline or its *Ac* derivative, m.p. 104—105°. Dehydrogenation (Pd–C) of (I) at 190—200° gives considerable amounts of amorphous products, 6 : 7-dimethoxy-1-methyl*iso*quinoline, m.p. 106—107° (picrate, m.p. 266—267°), and emetamine, 2 forms m.p. 138—139° and 153—154°, $[\alpha]_D^{0}$ +11·1° in abs. EtOH (picrate, m.p. 149—151°). M.p. are corr. (block); limit of error ±2°. H. W.

Steroids and sex hormones. XCII. Stereoisomeric dihydrosolanidines. V. Prelog and S. Szpilfogel (*Helv. Chim. Acta*, 1944, **27**, 390—400).—The isolation of four stereoisomeric dihydrosolanidines and of the two corresponding saturated parents emphasises the stereochemical similarity of solanidine (I) and cholesterol and strengthens the probability that (I) is (*A*). (I) is hydrogenated (PtO_2 in AcOH) to solanidan-3(β)-ol (II), m.p. 220°


(*A*.)

196°, $[\alpha]_D^{18}$ +16·5°±2°; p-*toluenesulphonate* (III), m.p. 169·5—170°). (II) is oxidised [Al(OPh)$_3$–$COMe_2$–C_6H_6] to solanidan-3-one, m.p. 210—212°, $[\alpha]_D^{17}$ +45·8°±2°, hydrogenated (PtO_2–AcOH) to (II) but converted by similar hydrogenation with addition of HBr into a solanidanol acetate, m.p. 190°, $[\alpha]_D^{17}$ +18·0°±2°, hydrolysed by boiling KOH–MeOH to *solanidan*-3(α)-*ol* (IV), m.p. 211—212·5°, $[\alpha]_D^{18}$ +31·9°±4° (*acetate*, m.p. 174—176°, $[\alpha]_D^{15}$ +21·9°±3°), which does not give a ppt. with digitonin. The proof that (IV) is epimeric with (II) with respect to $C_{(3)}$ is furnished by the production of (IV) by treatment of (III) with NaOAc and subsequent alkaline hydrolysis. (II) and (IV) are converted by B_2O_3 at 290—200°/high vac. into Δ^2- (or Δ^3-)solaniden, m.p. 165°, $[\alpha]_D^{17}$ +67·9°±1°, which is hydrogenated to solanidan, m.p. 161·5—162·5°, $[\alpha]_D^{17}$ +33·1°±2°. (I) is transformed by Al(OBu^t)$_3$ in boiling COMe$_2$ into Δ^4-solaniden-3-one, m.p. 213—216·5°, $[\alpha]_D$ +89·0°±1°, also obtained by use of Al(OPh)$_3$. This is hydrogenated (platinised Raney Ni in an alkaline medium) to allo*solanidan*-3(β)-*ol*, m.p. 216—217·5°, $[\alpha]_D^{17}$ +27·9°±2° (*acetate*, m.p. 140—141°, $[\alpha]_D^{18}$ +31·4°±3°), and allo*solanidan*-3(α)-*ol*, m.p. 212—214°, $[\alpha]_D^{18}$ +34·5°±3° (*acetate*, m.p. 140—141·5°, $[\alpha]_D^{18}$ +45·2°±3°). Further cryst. products could not be obtained from the residues but the presence of one of the solanidan-3-ols is established by epimerisation (Na in boiling xylene) followed by pptn. with digitonin, whereby (II) is isolated. B_2O_3 at 300°/high vac. transforms the *allo*-alcohols into Δ^2- (or Δ^3-)allo*solaniden*, m.p. 145·5—146·5°, $[\alpha]_D^{20}$ +34·0°±3°, hydrogenated (PtO_2 in AcOH) to allo*solanidan*, m.p. 140—142°, $[\alpha]_D^{18}$ +34·8°±4°. M.p. are corr. $[\alpha]_D$ are in $CHCl_3$. H. W.

VIII.—ORGANO-METALLIC COMPOUNDS.

Stereochemistry of organic derivatives of phosphorus. I. Synthesis of acidic and basic dissymmetric tertiary phosphines. Optical resolution of phenyl-*p*-(carbomethoxy)phenyl-*n*-butylphosphine sulphide. W. C. Davies and F. G. Mann (*J.C.S.*, 1944, 276—283).—*p*-$C_6H_4Br{\cdot}PCl_2$ and $HgPh_2$ in N_2 give *phenyl*-p-*bromophenyl-chlorophosphine* (I), b.p. 203—204°/11 mm., which with Cl_2 followed by H_2O affords the *-phosphonic acid*, m.p. 174·5°, and with MgEtBr yields the *-ethylphosphine*, b.p. 136—138°/0·05 mm. MgBr·$C_6H_4{\cdot}NMe_2$ (special conditions of prep.) with (I) leads to *phenyl*-p-*bromophenyl*-p-*dimethylaminophenylphosphine* (II), m.p. 107—108° (also obtained by using the Li derivative), which with S in CS_2 forms the *sulphide*, m.p. 126°. The *methiodide*, m.p. 158—159°, of this sulphide is produced with difficulty and reacts to give the *metho*-d-*camphorsulphonate*, m.p. 224—226° (decomp.), *methobromide Me alcoholate*, m.p. 145°, and *metho*-d-α-*bromocamphorsulphonate*, m.p. 198—199°, which could not be resolved. *Phenyl*-p-*bromophenyl*-p-*dimethylaminophenylphosphine selenide* has m.p. 135·5—136·5°. Mg 2-bromopyridine with (I) affords *phenyl*-p-*bromophenyl*-2-*pyridylphosphine*, m.p. 90—91° (*picrate*, m.p. 132°), converted into the *sulphide*, m.p. 109° [*methiodide*, m.p. 132—134° (decomp.)], which is too weakly

basic for salt formation, as is also the *sulphide*, m.p. 115—116°, of the -3-*pyridyl* derivative [*picrate*, m.p. 143—144° (decomp.)]. *p*-OMe·C_6H_4·PCl_2 (**III**) with MgEtBr gives *p*-anisyldiethylphosphine (methiodide, m.p. 132—133°, lit. 91°), which is hydrolysed (HI) to the p-*hydroxyphenyl* compound, b.p. 168—176°/19 mm. (*methiodide*, m.p. 168—169°). $HgPh_2$ and (**III**) yield *phenyl*-p-*anisyl-chlorophosphine* (**IV**), b.p. 137°/0·03 mm., which with $MgBu^aBr$ leads to the -n-*butylphosphine*, b.p. 139—141°/0·025 mm. This after hydrolysis (HI) with BzCl gives *phenyl*-p-*benzoyloxyphenyl*-n-*butylphosphine*, m.p. 91° (*oxide*, m.p. 136°), which forms the *sulphide*, m.p. 66—67°, hydrolysed to the *hydroxysulphide*, m.p. 97—98°. This sulphide condenses with $CH_2Br·CO_2Et$ to phenyl-*p*-(carboxymethoxy)phenyl-*n*-butylphosphine sulphide, which with *d*-CHPhMe·NH_2Cl gives the salt, cryst. to the d-α-*phenylethylamine* salt of the *sulphide*, m.p. 209—210°, decomposed (H_2SO_4) to the *l*-sulphide, −9·7° in C_6H_6 (l-NH_4 salt). From the mother-liquor is obtained the l-*amine* d-*acid* salt, m.p. 209—210°, decomposed to the *d*-sulphide, $[M]_D^{16}$ +9·6° in C_6H_6 (d-NH_4 salt, $[M]^{16}$, +12·2° in H_2O).

MgEtBr and (**IV**) give *phenyl*-p-*anisyl-ethylphosphine*, b.p. 137°/0·1 mm. (*methiodide*, m.p. 114—115°), hydrolysed to the -p-*hydroxyphenyl* compound, b.p. 160—175°/0·1 mm. (*Bz* derivative, m.p. 79—80°; *benzoyloxyphosphine sulphide*, m.p. 83—84°), which with S followed by $CH_2Br·CO_2Et$ leads to *phenyl*-p-(*carboxymethoxy*)*phenylethylphosphine sulphide*, m.p. 84° (*Na* salt; l-*phenylethylamine* salt, m.p. 206—207°; d-sec.-*butylamine* salt, m.p. 189—190°; d-*aminocamphor* salt, m.p. 166—168°), which could not be resolved. $MgPr^aBr$ and (**IV**) yield *phenyl*-p-*anisyl*-n-*propylphosphine*, b.p. 163·5°/0·3 mm. (*methiodide*, m.p. 114°), which with $MgBr·C_6H_4Me$ affords the -p-*tolylphosphine*, m.p. 116—118° (p-*chlorophenacyl bromide*, m.p. 199°). *Phenyl*-p-*bromophenyl*-p-*anisylphosphine*, m.p. 71°, is similarly prepared. NH_4 palladochloride and (**II**) give *dichlorobis*(*phenyl*-p-*bromophenyl*-p-*dimethylaminophenylphosphine*)-*palladium*, partial m.p. 247—249°. *Dichlorobis*(*phenyl*-p-*bromophenylethylphosphine*)*palladium*, m.p. 172·5—174° (decomp.), is similarly prepared and both compounds appear to be homogeneous. PCl_3 and Mg 2-bromopyridine give *tri*-2-*pyridyl-phosphine*, m.p. 113—114°; the -*arsine*, m.p. 85°, is similarly obtained. The compounds are formulated *abc*P→X, where *a*, *b*, and *c* are unlike aryl or alkyl groups, and X is oxide, sulphide, or selenide, and one compound has been resolved. F. R. S.

Sulphides and sulphones derived from *p*-thiolphenylarsonic acid. J. F. Morgan and C. S. Hamilton (*J. Amer. Chem. Soc.*, 1944, **66**, 874—875).—*p*-$NH_2·C_6H_4·[CH_2]_2·OH$ (prep. from the NO_2-compound by H_2–Raney Ni in $COMe_2$), m.p. 43—44°, b.p. 232—235° (decomp.)/38 mm. (*hydrochloride*, m.p. 170°), gives (Bart) p-β-*hydroxyethylthiolphenylarsonic acid*, dimorphic, m.p. 120·5—121° and 132—133°. *p*-$AsO_3H_2·C_6H_4·SCN$ in boiling 10% NaOH gives an acid, ? *p*-$SH·C_6H_4·AsO_3H_2$, which with the appropriate halide in boiling NaOH–H_2O or –EtOH yields p-γ-*hydroxy*-n-*propyl*-, m.p. 116·3—117·5°, p-β-*ethoxyethyl*-, m.p. 121—122°, p-β-β′-*hydroxyethoxyethyl*- (*Na* salt, m.p. >250°), p-*acetonyl*-, m.p. 172·5°, *p*-carboxymethyl- (**I**), m.p. 192° (lit. 187°, 248—250°). p-*carbethoxymethyl*-, m.p. 123° [some (**I**) is also obtained], and *p*-2′-*amino*-4′-*pyrimidyl*- (**II**), m.p. 131·5—132°, -*thiolphenylarsonic acid* and 4-*nitro*-, m.p. 183°, and thence (H_2–Raney Ni in aq. $NaHCO_3$) 4-*amino*-4′-*arsonodiphenyl sulphide*, m.p. 211·5° (decomp.). 27·5% H_2O_2 oxidises these compounds [except (**II**), which decomposes] to p-β-*hydroxyethane*-, m.p. 177°, p-γ-*hydroxypropane*-, m.p. 160·5°, p-β-*ethoxyethane*-, m.p. 182·5—184·5°, *p*-β-β′-hydroxyethoxyethane- (*Na* salt, m.p. 180·5°), p-*acetone*-, m.p. 202·5—203·5°, p-*carboxymethane*-, m.p. 188—189°, and p-*carbethoxymethane*-, m.p. 165—166°, -*sulphonylphenylarsonic acid* and 4-*nitro*-, m.p. >250°, and 4-*amino*-4′-*arsonodiphenyl sulphone*, m.p. 229—230° (decomp.). M.p. are determined in a preheated bath to minimise anhydride formation. R. S. C.

Factors determining the course and mechanism of Grignard reactions. XIV. Replacement of halogen atoms of aromatic halides with hydrogen atoms by the action of Grignard reagents and cobaltous chloride. M. S. Kharasch, D. C. Sayles, and E. K. Fields (*J. Amer. Chem. Soc.*, 1944, **66**, 481—482; cf. A., 1944, II, 223).—In presence of 5 mol.-% of $CoCl_2$, dihalogenated C_6H_6 derivatives are reduced by MgRBr (R = Me, Et, or Ph) in Et_2O to the monohalogenated compound (usually 40—55%) or, if a large excess of MgRBr is used, to the hydrocarbon; polymerides are also formed. Polycyclic aryl bromides with $MgBu^aBr$ give 44—62% of hydrocarbon, but *p*-C_6H_4PhBr gives also 1·3% of dixenyl. Use of MgPhBr gives also much Ph_2. Mg *p*-xenyl or 9-phenanthryl bromide with EtBr and $CoCl_2$ gives 100% of dixenyl and diphenanthryl, respectively. A free radical mechanism is postulated. R. S. C.

Gallium trimethyl—See A., 1944, I, 182.

IX.—PROTEINS.

Methylation and acetylation of wool, silk fibroin, collagen, and gelatin. S. Blackburn and H. Phillips (*Biochem. J.*, 1944, **38**, 171—178; cf. B., 1941, II, 338).—Acetylation of wool with Ac_2O diminishes the extent of subsequent methylation of free CO_2H by Me_2SO_4, MeBr, or MeI. When wool and silk fibroin are treated with Ac_2O in MeOH, methylation of free CO_2H groups and *N*- and *O*-acetylation occur simultaneously. Peptide methylation of wool and esterification of its free CO_2H are not prevented by previous treatment with borax, HNO_2, or CH_2O. Esterification is increased if amide groups are removed by acid hydrolysis. Me_2SO_4 esterifies free CO_2H and causes peptide methylation of collagen, H_2SO_4 becoming covalently linked to proteins. When MeBr or MeI replaces Me_2SO_4, esterification occurs but peptide methylation takes place slowly or not at all. W. McC.

Reaction of casein with formaldehyde. V. Behaviour of the ε-amino-group of lysine and of the peptide groups. H. Nitschmann and H. Hadorn (*Helv. Chim. Acta*, 1944, **27**, 299—312).—The ε-NH_2 of lysine (**I**) is primarily involved in the action of CH_2O on casein (**II**) at pH 5·6 and room temp. Comparison of the abilities of deaminated and ordinary (**II**) to unite with CH_2O and the diminution of the Van Slyke N caused by CH_2O tanning indicate that CH_2O and the free NH_2 of (**I**) react in the ratio 1 : 1. It is established that the amount of H_2O formed is equiv. to the CH_2O which reacts with (**I**). In addition to the NH_2 of (**I**), other groups are present in (**II**) which react with CH_2O in a weakly acid medium. These are probably peptide groups but their reaction with CH_2O is not accompanied by condensation, at any rate in the cold. The tanning action of CH_2O (loss of solubility; diminution of the ability to swell) appears to depend on the formation of CH_2 bridges between the NH_2 of (**I**) and the peptide groups whereby the protein mols. are united by main valencies. H. W.

Blue chromo-protein of eggs of goose-barnacle.—See A., 1944, III, 537.

X.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Fundamental chemistry of lignin. K. Freudenberg (*Svensk Kem. Tidskr.*, 1943, **55**, 20; *Chem.-Ztg.*, 1944, **68**, 39—42).—A lecture. R. S. C.

Colour reactions of lignin and their use in analytical chemistry. P. M. Isakov (*J. Appl. Chem. Russ.*, 1943, **16**, 234—240).—Drop reactions on newspaper paper (containing lignin) are different from those on filter-paper. Solutions of $AuCl_3$ give a black and of NH_4VO_3 a greenish-black spot. $SnCl_2$ and H_2PtCl_6 produce a stable orange spot. $SnCl_2$ and $AgNO_3$ form first AgCl and then Ag which is dissolved by $Hg(NO_3)_2$ solution. Picric acid and SnCl. form picramic acid. $Co(NO_3)_2$ gives a stable blue spot with KCNS and an azure spot with picric acid. $Fe(NO_3)_3$ and $K_3Fe(CN)_6$ give Turnbull's blue. Aq. NH_2Ph gives a yellow and aq. benzidine an orange coloration. Dil. HNO_3 can be used as a sympathetic ink. J. J. B.

Constitution of shellac. Increased yield of aleuritic acid. B. S. Gidvani (*J.C.S.*, 1944, 306).—By a new method of separation, the yield of aleuritic acid has been increased to nearly 43%. The previous formulæ for shellac resin may not be correct and shellolic acid is possibly not a primary product of hydrolysis. F. R. S.

Dyes from *Ammothamnus lehmanni*, Bge. A. Sadikov and G. Lazurevski (*J. Gen. Chem. Russ.*, 1943, **13**, 309—313).—The crude dye from this Central Asiatic plant (obtained by extraction with alkali and acidification of the extract, in 14% yield from roots, 4% from stems and leaves), after fractional extraction with alkali, was divided into two parts by extraction with EtOAc. The sol. part, after purification by pptn. from EtOH, yielded an orange-red amorphous *compound*, $C_{16}H_{22}O_4$ (**I**), m.p. 96—98° (*Ac*$_2$ derivative, m.p. 107—109°); the insol. portion, recryst. from EtOH, yielded dark red plates, decomp. >360°, of an acidic *compound* (**II**), probably $C_{16}H_{22}O_7N_2$. (**I**) is pptd. from faintly alkaline solution by CO_2 and gives a dark green coloration with $FeCl_3$; distillation of (**I**) with Zn dust gave no recognisable products, oxidation with alkaline $KMnO_4$ gave $H_2C_2O_4$, and fusion with NaOH yielded phloroglucinol and AcOH. The similarity of (**I**) and tetrahydro-α-mangostene is indicated. (**I**) and (**II**) are acid dyes, satisfactory for silk. R. C. P.

Chemical examination of root of *Centaurea behen* (Linn.). P. N. Bhargava and S. Dutt (*Proc. Indian Acad. Sci.*, 1944, **19**, A, 163—166).—Extraction of the root of *C. behen* ("behman") with EtOH affords "*behmin*," $C_{23}H_{45}O_2·OMe$, sinters 72°, m.p. 79—80° (*tetrabromide*, m.p. 67°), which has properties of a $\Delta^{\alpha\beta}$-unsaturated lactone.

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A II—Organic Chemistry.

OCTOBER, 1944.

I.—ALIPHATIC.

Production of ethylene from [hydrocarbon] oil.—See B., 1944, II, 218.

Reaction of dibromides of mono-substituted ethylenes with potassium iodide.—See A., 1944, I, 226.

***n*-Nonatriacontane.** E. Stenhagen and B. Tagtstrom (*J. Amer. Chem. Soc.*, 1944, **66**, 845—846).—*n*-$C_{18}H_{37}I$, $CO(CH_2{\cdot}CO_2Et)_2$, and Na in boiling Bu$^{\alpha}$OH give an ester, converted in boiling, conc. HCl into n-*nonatriacontan-υ-one*, m.p. 91·1—91·4° [long *X*-ray spacing (melted specimen) 51·5 A.], reduced (Clemmensen) to n-*nonatriacontane*, dimorphic (transition point ~75°), m.p. 80·0—80·2° (long *X*-ray spacings 51·3 and 47·1 A.). R. S. C.

Hydrolysis of trimethylethylene dibromide [βγ-dibromo*iso*pentane]. Mechanism of ketone formation. C. M. Suter and H. D. Zook (*J. Amer. Chem. Soc.*, 1944, **66**, 738—742).—Conversion of βγ-dibromo*iso*pentane (prep. from $CMe_2{:}CHMe$ by Br–CCl_4 at 10—20° or, much less well, from $CMe_2Et{\cdot}OH$ by Br), m.p. 12—13°, b.p. 59·5—61°/19 mm., into $COMePr^{\beta}$ is shown to proceed by way of $CHMeBr{\cdot}CMe_2{\cdot}OH$ and possibly $OH{\cdot}CHMe{\cdot}CMe_2{\cdot}OH$ by measuring the rates of hydrolysis in H_2O and aq. dioxan. The same may also hold for $CH_2Br{\cdot}CMe_2Br$. R. S. C.

Preparation of pure octyl alcohol and methyl *n*-hexyl ketone.—See B., 1944, II, 218.

Configuration of the βγ-butylene glycols. S. A. Morell and A. H. Auernheimer (*J. Amer. Chem. Soc.*, 1944, **66**, 792—796).—Reactions described below prove the configurations assigned. Heating *L*(+)-$(CHMe{\cdot}OH)_2$, b.p. 180—182°/745 mm., α {$[\alpha]_D$ (homogeneous) here and below} +1·06°, with Ac_2O, C_5H_5, and a little H_2SO_4 gives *L*(−)-$(CHMe{\cdot}OAc)_2$, b.p. 190—192°/745 mm., α −0·60° (cf. Winstein *et al.*, A., 1939, II, 401), which, when passed over stainless steel at 595°, yields $(CH_2{:}CH)_2$, AcOH, and *L*(−)-$CH_2{:}CH{\cdot}CHMe{\cdot}OAc$, b.p. 111·5—113·5°/745 mm., α −1·71°. Hydrolysis by aq. NaOH at 100° then gives *L*(+)-$CH_2{:}CH{\cdot}CHMe{\cdot}OH$, b.p. 96·2—96·5°/745 mm., α +0·68°, hydrogenated (PtO_2) at 45 lb. to *L*(+)-$CHMeEt{\cdot}OH$, b.p. 99—100°/745 mm., α +0·24° (cf. Kenyon *et al.*, A., 1925, i, 771). *DL*-$CH_2{:}CH{\cdot}CHMe{\cdot}OH$, b.p. 96·0—96·5°/745 mm., gives similarly *DL*-$CHMeEt{\cdot}OH$, b.p. 99—100°/745 mm. *D*(−)-$(CHMe{\cdot}OH)_2$ (**I**), α −12·85°. gives, as above, *D*(+)-$(CHMe{\cdot}OAc)_2$ (**II**), α +1·35°, and thence *D*(−)-$CH_2{:}CH{\cdot}CHMe{\cdot}OH$, α −1·28°. Whereas in H_2SO_4–Ac_2O–C_5H_5, (**I**), α −12·99°, is partly racemised to yield (**II**), α +4·98°, in Ac_2O alone at 100° it gives (**II**), α +13·73°, whence NaOH–MeOH–H_2O regenerates (**I**), α −12·95°, thus rendering Walden inversion during acetylation very improbable. *d* and *n* are given for these substances. R. S. C.

Optical isomerides of butane-βγ-diol produced by fermentation.—See A., 1944, III, 696.

Organ extracts. VI. Isolation of chimyl alcohol (*d*-α-hexadecylglycerol) from testes extract and its identity with "testriol." V. Prelog, L. Ruzicka, and F. Steinmann (*Helv. Chim. Acta*, 1944, **27**, 674—677).—The isolation of chimyl alcohol, m.p. 64°, $[\alpha]_D$ +2·5° in $CHCl_3$ (diphenylurethane, m.p. 97·5—98·5°; di-*p*-nitrobenzoate, m.p. 59—60°, $[\alpha]_I^{16}$ −29·8° in $CHCl_3$), is described (cf. Baer and Fischer, A., 1941, II, 311). Oxidation by $Pb(OAc)_4$ gives CH_2O and hexadecoxyacetaldehyde (*oxime*, m.p. 79—80°). The alcohol is identical with the "testriol" of Hirano (*J. Pharm. Soc. Japan*, 1936, **56**, 122), which therefore has not the structure $OH{\cdot}CMe_2{\cdot}[CH_2]_{14}{\cdot}CH(OH){\cdot}CH_2{\cdot}OH$ assigned by him. All optically active α-glyceryl ethers have the same configuration whatever their source. H. W.

βδ : γε-Dimethylene-*DL*-xylitol and βδ-methylenexylitol. R. M. Hann, A. T. Ness, and C. S. Hudson (*J. Amer. Chem. Soc.*, 1944, **66**, 670—673).—*DL*-Xylitol with 37% aq. CH_2O–conc. HCl at 50° gives γε-*dimethylene*-DL-*xylitol* (**I**), m.p. 201—202° (crystallo-optical data of this and the *L*-isomeride given) [α-*acetate*, m.p. 156—157° (crystallographic data); α-*benzoate*, m.p. 164—165°; α-*carbanilate*, m.p. 196—197°], the α-p-*toluenesulphonate*, m.p. 145—146°, of which with NaI in, best, CH_2Ac_2 at 120° or boiling Ac_2O gives the α-*iodide*, m.p. 144—145°. H_2–Raney Ni reduces this in KOH–MeOH at 22° to βδ : γε-*dimethylene*-α-*deoxy*-DL-*xylitol*, m.p. 155—156°, also obtained from βγ : δε-di*iso*propylidene-α-deoxy-*DL*-xylitol by conc. HCl–CH_2O–H_2O at 50°. With H_2SO_4 in AcOH–Ac_2O at 5°, (**I**) gives γ-*acetoxymethyl*-βδ-*methylene*-DL-*xylitol* αε-*diacetate*, m.p. 138—139°, which consumes 3 mols. of aq. NaOH and in NaOMe–MeOH–$CHCl_3$ gives βδ-*methylene*-DL-*xylitol*, m.p. 108—109° (*triacetate*, m.p. 87—88°; *tribenzoate*, m.p. 117—118°; *tri*-p-*toluenesulphonate*, m.p. 198—199°) (cf. following abstract), converted by BzCl–C_5H_5N at 25° into the αε-*dibenzoate*, m.p. 139—140°, but unaffected by aq. $NaIO_4$ (proof of structure). R. S. C.

Acetolysis of trimethylene-*D*-sorbitol. βδ-Methylene- and αγ : βδ-dimethylene-*D*-sorbitol. A. T. Ness, R. M. Hann, and C. S. Hudson (*J. Amer. Chem. Soc.*, 1944, **66**, 665—670).—Structures assigned below are proved by the reactions recorded. They prove that acetolysis of $CH_2{:}$ derivatives of sugar-alcohols occurs where the $CH_2{\cdot}O$ is linked to a primary C (cf. A., 1944, II, 118). *D*-Sorbitol, 37% aq. CH_2O, and conc. HCl at 50° give (? αγ : βδ : εζ-)trimethylene- (**I**) (68%), m.p. 212—216°, $[\alpha]_D^{20}$ −30·8° in $CHCl_3$, and αγ : βδ-*dimethylene*-D-*sorbitol* (**II**) (8%), m.p. 174—175°, $[\alpha]_D^{20}$ −29·6° in H_2O (cf. Schulz *et al.*, A., 1894, i, 438). With a little conc. H_2SO_4 in AcOH–Ac_2O, (**I**) gives γε-*di*(*acetoxymethyl*)-βδ-*methylenesorbitol* αζ-*diacetate*, m.p. 111—112°, $[\alpha]_D^{20}$ +29·8° in $CHCl_3$, which consumes 4 mols. of NaOH and with 0·2N-NaOMe–MeOH in $CHCl_3$ at 5° gives βδ-*methylene*-*D*-*sorbitol* (**III**), m.p. 163—164°, $[\alpha]_D^{20}$ −9·8° in H_2O (*tetra-acetate*, m.p. 150—151°, $[\alpha]^{20}$ −1·5° in $CHCl_3$). (**III**) consumes 1 mol. of $Pb(OAc)_4$–AcOH, aq. $NaIO_4$, or HIO_4. With HIO_4 it gives 0·85 mol. of CH_2O and a reducing sugar, which with H_2–Raney Ni at 100°/133 atm. yields βδ-*methylene*-*D*-*xylitol*, m.p. 108—109°. In Ac_2O–C_5H_5N at 25° (**II**) gives the εζ-*diacetate*, m.p. 135—136°, $[\alpha]_D^{20}$ −12·8° in $CHCl_3$, in BzCl–C_5H_5N gives the εζ-*dibenzoate*, m.p. 134—135°, $[\alpha]_D^{20}$ −54·8° in $CHCl_3$, and in aq. $NaIO_4$ (1 mol. consumed) at 25° gives 0·98 mol. of CH_2O and aldehydo-αγ : βδ-*dimethylene*-L-*xylose*, $+H_2O$ (lost at 140—145°/vac.) (**IV**), sinters 150°, m.p. 175—180°, and anhyd., m.p. 189—192°, $[\alpha]_D^{20}$ −38·7° in H_2O (*oxime*, m.p. 227—228°, $[\alpha]_D^{20}$ −272° in C_5H_5N, −215·0° in H_2O). H_2–Raney Ni reduces (**IV**) in H_2O at 25° to βδ : γε-*dimethylene*-L-*xylitol* (**V**), m.p. 217—219°, $[\alpha]_D^{20}$ −25·3° in H_2O [α-*acetate*, m.p. 153—154°, $[\alpha]_D$ +2·8° in $CHCl_3$ (crystallo-optical data given)], which in H_2SO_4–Ac_2O–AcOH at 0° gives γ-*acetoxymethyl*-βδ-*methylenexylitol* αε-*diacetate*, m.p. 139—140°, α 0; the derived αεζ-*triacetate*, m.p. 94—95°, $[\alpha]_D^{20}$ +11·0° in $CHCl_3$, with NaOMe–MeOH–$CHCl_3$ gives (**III**). CH_2O–HCl converts (**V**) into (**I**) (m.p. 210—214°). R. S. C.

αγ : βδ-Dibenzylidene-*D*-sorbitol. S. J. Angval and J. V. Lawler (*J. Amer. Chem. Soc.*, 1944, **66**, 837—838).—βδ-Benzylidene-*D*-sorbitol (A., 1935, 1104) has m.p. 176—177°, $[\alpha]_D^{17}$ −1·1° in H_2O, and is obtained (17% yield) from αγ : βδ-dibenzylidene-*D*-sorbitol (**I**) (A., 1942, II, 390) by hot AcOH–EtOH–H_2O, thus proving the structure of (**I**). The structure of αγ : βδ : εζ-tribenzylidene-*D*-sorbitol, dimorphic, m.p. 203° and ~195—199° (190°) (cf. A., 1937, II, 83), is proved by similar hydrolysis to (**I**) [εζ-diacetate, m.p. 208—209° or between 202° and 206° (lit. 201—204°)]. Meunier's $(CHPh{:})_2$ compound, m.p. 162° (A., 1889, 479), was a mixture. M.p. are corr. R. S. C.

Volemitol hepta-acetate. W. D. Maclay, R. M. Hann, and C. S. Hudson (*J. Org. Chem.*, 1944, **9**, 293—297).—Treatment of natural or synthetic volemitol [*D*-manno-*D*-*talo*heptitol] with Ac_2O and NaOAc gives almost quantitatively volemitol hepta-acetate (**I**), m.p. 63°, $[\alpha]_D^{20}$ +36·1° in $CHCl_3$, +30·8° in glacial AcOH, identical with the product of Bougault *et al.* (A., 1903, i, 62), de-acetylated to pure volemitol (**II**). The compound described by Bourquelot (A., 1896, i, 273) and by Ettel (A., 1933, 47) is mannitol hexa-acetate (**III**). Photomicrographs of (**I**) and (**III**) are given. Directions are given for the isolation of (**II**) from the mixture of it with *D*-perseitol which results from the reduction of *D*-mannoheptulose. H. W.

Polymerisation of simple vinyl ethers. Vinyl *iso*butyl ether. M. F. Schostakovski and F. P. Sidelkovskaja (*J. Gen. Chem. Russ.*, 1943, **13**, 428—435).—Polymerisation of $Bu^{\beta}O{\cdot}CH{:}CH_2$ can be effected by BF_3,Et_2O, $FeCl_3$, $AlCl_3$, $ZnCl_2$, $SnCl_4$, I, or anhyd. $SnCl_2$; $SnCl_2$ (2 wt.-% on the ether) gives a polymer of mol. wt. (by η in C_6H_6) 1795—2000, separated into fractions of differing mol. wt. by pptn. from C_6H_6 with MeOH. The total polymer gives with aq. 20% HNO_3 at 100°/12 hr. $H_2C_2O_4$ and a liquid product, b.p. 97—105°, whilst with Na in $Bu^{\gamma}OH$, followed by treatment with H_2O, it gives polyvinyl alcohol (?), η_{sp} 0·2325, mol. wt. (η) 5280. F. H.

Acetylenic ethers. IV. Hydration. T. L. Jacobs and S. Searles, jun. (*J. Amer. Chem. Soc.*, 1944, **66**, 686—689; cf. A., 1943, II, 89).—Rates of hydration of CH·C·OR (*A*) (R = Et, Bu, and Ph) are measured dilatometrically in H_2O or 12·5—42·7% EtOH at 25° and pH 2·255—6·47. The reaction is of first order with respect to [*A*] and $[H_3O^+]$. The mechanism is: $(A) + H_3O^+ \rightarrow (CH_2{:}C{\cdot}OR)^+$; $(B) + H_2O \rightarrow [CH_2{:}C(OR){\cdot}OH_2]^+ \rightarrow (+H_2O)$ $CH_2{:}C(OR){\cdot}OH$ $(C) + H_3O^+$; $(C) \rightarrow$ ROAc. R. S. C.

Unsaturated synthetic glycerides. VI. Polymorphism of *s*-mono-oleyl-disaturated triglycerides. B. F. Daubert and T. H. Clarke (*J. Amer. Chem. Soc.*, 1944, **66**, 690—691; cf. A., 1944, II, 211).—Heating and cooling curves yield the following transition points: α-monostearin, forms I 81·8°, II 78·0°, III 25·4°, IV 48·5° (Malkin's β, β′, α, and γ forms, respectively); α-monomyristin, forms I 71·0°, II 67·5°, III 55·3°, IV 21·3°; glyceryl β-oleate αγ-diacylate in which the acyl is stearyl, forms I 41·6°, II 37·0—37·6°, III 29·8°, IV 22·3°, palmityl, forms I 35·2°, II 30·4°, III 20·8°, IV 12·0°, myristyl, forms I 26·3°, II 21·5°, III 12·3°, IV 2·1°, dodecoyl, forms I 16·5°, II 11·0°, III 1·4°, IV −7·1° to −7·5°, and *n*-decoyl, forms I 6·2°, II 0·6, III −10·2°, IV −16·4°. R. S. C.

Ester interchange. H. J. Wright, J. B. Segur, H. V. Clark, S. K. Coburn, E. E. Langdon, and R. N. DuPuis (*Oil and Soap*, 1944, **21**, 145—148).—The application of ester-interchange reactions to triglycerides, *e.g.*, the formation of fatty acid esters of MeOH, EtOH, PrOH, $OH{\cdot}[CH_2]_2{\cdot}O{\cdot}CH_2Ph$, polyhydric alcohols, furfuryl alcohol, etc., and liberation of glycerol by interaction of glyceride and the alcohol (or Me esters and polyhydric alcohols) in presence of Pb or alkaline salts as catalyst, is briefly reviewed. A continuous method of production, viz., mixing glyceride, MeOH, and NaOH catalyst at 65° for 5 min. and then centrifuging, yielded 85% of the theoretical glycerol. The utilisation of, *e.g.*, the Me and Et esters (which are obtained very pale) in soap-making, and of other esters as possible plasticisers for lacquers and synthetic rubbers, or the furfuryl esters for resin formation, is considered. E. L.

Preparation of ethyl ε-bromo-*n*-hexoate. G. B. Brown and C. W. H. Partridge (*J. Amer. Chem. Soc.*, 1944, **66**, 839).—*cyclo*-Hexanone and $K_2S_2O_8$ (cf. Robinson *et al.*, A., 1937, II, 196) give *n*-hexo-ε-lactones, converted by 48% HBr–conc. H_2SO_4 at room temp. and then 100° and finally by boiling H_2SO_4–EtOH into $Br{\cdot}[CH_2]_5{\cdot}CO_2Et$ (45—55% over-all), b.p. 120—125°/14 mm. R. S. C.

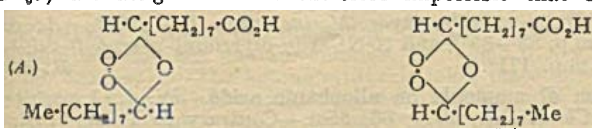
Polymerisation of undecenoic acid in presence of boron fluoride. J. R. Cann and E. D. Amstutz (*J. Amer. Chem. Soc.*, 1944, **66**, 839—840).—Undecenoic acid and gaseous BF_3 at room temp. give an oily polymer having reduced I val. and acid val., much of the CO_2H being "esterified" with the C:C. After hydrolysis the polymer gives a CHI_3 test, proving this interpretation. $CHMe{:}CH{\cdot}CO_2H$ and fatty acids from drying oils behave similarly. R. S. C.

Reformatsky condensations involving vinylogues of halogenoacetic esters. II. Methyl γ-bromosenecioate. R. C. Fuson and P. L. Southwick (*J. Amer. Chem. Soc.*, 1944, **66**, 679—681; cf. A., 1938, II, 442).—A method of lengthening a C chain by an isoprene unit is described. $CH_2{:}CMe{\cdot}CH_2Cl$ and CuCN (cf. Tamele *et al.*, A., 1941, II, 82) give *β-methylallyl cyanide* (76%), b.p. 134·5—136·5°, which with Br–$CHCl_3$ (cooling) yields *βγ-dibromoisovaleronitrile*, b.p. 89°/2—3 mm., converted by K_2CO_3 in boiling COMeEt into *γ-bromosenecionitrile* (~50%), b.p. 84°/8 mm., or by boiling H_2SO_4–MeOH [5 : 8 (vol.)] into *Me βγ-dibromoisovalerate*, b.p. 84—85°/3 mm. With K_2CO_3 in boiling COMeEt this gives impure $CH_2Br{\cdot}CMe{:}CH{\cdot}CO_2Me$ (**I**), b.p. 63—66°/3 mm., better obtained by the method of Ziegler *et al.* (A., 1943, II, 2, 32). PhCHO, (**I**), Zn, and a trace of I in boiling C_6H_6–Et_2O give esters, b.p. 146—148°/2—3 mm. and 152—176°/2—3 mm., hydrolysed (KOH–EtOH) to *δ-phenyl-β-methyl-Δ$^{\alpha\gamma}$-pentadienoic acid, forms* A, m.p. 158·5—159·5°, and B, m.p. 156·5—157·5°, respectively (cf. *loc. cit.*). Form *B* is accompanied by some *δ-phenyl-β-methyl-Δ$^{\alpha}$-buteno-δ-lactone*, m.p. 61—62°. Form *A* is also obtained by condensing $CHPh{:}CH{\cdot}COMe$ and $CH_2Br{\cdot}CO_2Et$ by Zn and subsequently hydrolysing by KOH–EtOH. R. S. C.

Ozonides and their fission. A. Rieche, R. Meister, and H. Sauthoff [with, in part, H. Pfeiffer] (*Annalen*, 1942, **553**, 187—249).—Review of the properties of the ozonides and comparison with the alkyl peroxides confirms Staudinger's formulation, $CHR\langle^{O\cdot O}_{\ \ O}\rangle CHR$. Pure ozonides are best obtained by use of O_3 passed through 0·01N-NaOH and dried with P_2O_5. MeCl and EtCl are the most suitable solvents; CCl_4 and EtOAc are also useful but AcOH is unsuitable since it is very hygroscopic, difficult to remove, and causes hydrolysis. The ozonisation of $(CHMe)_2$ and C_2H_4 is described. In no case has there been any indication of a labile intermediate such as the "molozonide" of Staudinger. The physical properties of the ozonides are intermediate between those of the corresponding dialkyl and hydroxydialkyl peroxides. Refractometric measurements show that only one peroxide group is present in the ozonides, in which it exists in the same form as in the peroxides. Absorption curves permit only qual. conclusions but show close similarity in constitution between peroxides and ozonides. The parachor vals. indicate the presence of a 4- or 5-membered ring. Determination of active O in peroxides and ozonides is seldom quant. but for ozonides a val. in excess of that required for one active O has never been observed. The use of the acetal formula does not involve any essential alteration in the Harries scheme for the decomp. of ozonides. Examination of the more tractable ozonide (**I**) of oleic acid confirms Harries' observation of its decomp. by Fe into the peroxides of nonaldehyde and azelaicsemialdehyde. In AcOH these substances are unimol. but in freezing dioxan or boiling Et_2O or $COMe_2$ a double mol. wt. is observed. Fresh analyses, determination of active O, and observed decomp. essentially into 2 mols. of aldehyde and 1 mol. of H_2O_2 show that the compounds are respectively dihydroxynonyl peroxide $\{Me{\cdot}[CH_2]_7{\cdot}CH(OH){\cdot}O\}_2$ and the dicarboxylic acid $\{CO_2H{\cdot}[CH_2]_7{\cdot}CH(OH){\cdot}O\}_2$; the former has been obtained synthetically from nonaldehyde and H_2O_2. Similarly, Harries' "formaldehyde peroxide" is $(OH{\cdot}CH_2{\cdot}O)_2$. The first step in the fission of ozonides of *n*-olefines in the presence of H_2O is therefore the hydrolysis of the ether bridge. The invariable production of symmetrical dialdehyde peroxides and not mixed dihydroxyalkyl peroxides by the fission of ozonides is due to an exchange reaction since a hydroxyalkyl peroxide is shown to react with an aldehyde different from that contained in the peroxide with production of a symmetrical dihydroxyalkyl peroxide, $2OH{\cdot}CHR'{\cdot}O_2H + 2R''CHO \rightarrow (OH{\cdot}CHR'{\cdot}O)_2 + (OH{\cdot}CHR''{\cdot}O)_2$. Hydrolysis of ozonides is initiated by rupture of the ether ring. Dihydroxyalkyl peroxides are thus produced and form an equilibrium with hydroxyalkyl H peroxides, aldehyde, and H_2O_2. Hydroxyalkyl H peroxides yield carboxylic acids and H_2O. The ozonides of $(CAlk_2{\cdot})_2$ and $(CAr_2{\cdot})_2$ have a peculiar position. Direct conversion of olefines into carboxylic acids is possible when ozonisation occurs in a warm hydrolysing solvent, *e.g.*, aq. AcOH. Thus oleic acid is smoothly transformed into pelargonic and azelaic acid and undecenoic into sebacic and formic acid. Thermal fission of ozonides, usually in presence of a catalyst, occurs: $CHR\langle^{O\cdot O}_{\ \ O}\rangle CHR' \rightarrow R'CHO + CHR'O_2$ ($\rightarrow RCO_2H$) and $CR_2\langle^{O\cdot O}_{\ \ O}\rangle CHR' \rightarrow CR_2O_2{\cdot} + R'CHO$. Catalytic fission in presence of Fe^{II} salts, Ag, Pd, or Pt probably proceeds: $CHR\langle^{O\cdot O}_{\ \ O}\rangle CHR \rightarrow R{\cdot}C(:O){\cdot}O{\cdot}CHR{\cdot}OH \rightarrow RCO_2H + RCHO$; intramol. disproportionation accompanies hydrolysis and becomes the main reaction in anhyd. media. It appears probable that the weakening of the C–C union in the formation of ozonides depends on diradical formation and hence can be explained in the manner advanced by Criegee for the dehydrogenation of αβ-glycols. During the ozonisation of (**I**) in EtOAc or CCl_4, CH_4, CO, and CO_2 are evolved in amount corresponding to the shortening by 1 unit of 14% of the chain of (**I**); no theoretical explanation is advanced. $(OH{\cdot}CHMe{\cdot}O)_2$ is converted by P_2O_5 in dry Et_2O or MeCl into a peroxide, b.p. 27°/55 mm., identical with that derived by the ozonisation of $(:CHMe)_2$, thus directly establishing the structure of the ozonide; more complex compounds are obtained simultaneously.

Ozonisation of the simpler olefines gives viscous products which remain after removal of the monomerides and may form the main product if ozonisation is prolonged. The relatively small mol. wt. observed for these compounds in freezing AcOH is due to hydrolysis by the solvent, which increases with time; in C_6H_6, dioxan, and cineole much higher vals. are obtained so that the supposed "dimerides" are really polymerides which may contain a small proportion of dimerides. The latter are shown to exist by the isolation of dimeric butene ozonide $O(CHMe{\cdot}O{\cdot}O{\cdot}CHMe)_2O$ in addition to the monomeride from $(OH{\cdot}CHMe{\cdot}O)_2$ and P_2O_5, and of the cryst. highly explosive tetramethylene diperoxide from P_2O_5 and $(OH{\cdot}CH_2{\cdot}O)_2$. Most ozonisation products hitherto described in the literature as dimeric ozonides are multimol. and true dimeric products have thus far been isolated only by synthesis from dihydroxyalkyl peroxides. Determinations of mol. wt., parachor, mol. refraction, and ultra-violet absorption spectrum indicate that the viscous liquids, regarded previously as dimerides, are mixtures of multimol. ozonides containing as a mean 4—6 mols. Polymeric butene ozonide is therefore $CHMe\langle^{O_2-CHMe-O}_{[O{\cdot}CHMe{\cdot}O_2]_x}\rangle CHMe$. In the rings peroxide groups and ether bridges alternate, $\cdot O_2{\cdot}CR_2{\cdot}O{\cdot}CR_2{\cdot}O_2{\cdot}CR_2{\cdot}O{\cdot}CR'_2$, but the ring structure is not definitely established. Fission of the complex ozonides is essentially the same as that of the mono- and di-merides; thus butene ozonide and alkali give equimol. amounts of AcOH and MeCHO and alkali and mol. Ag cause decomp. with elimination of H. Complex butene ozonide like the dimeride becomes more viscous and gradually highly explosive and sensitive to trituration when kept in absence of moisture. At 80—90°/vac. this dangerous "cracking" is complete in 2 hr., leading to a compound $(C_2H_4O_2)_x$ in which all the O is peroxidic; MeCHO is evolved and the product appears to be polymeric ethylidene peroxide. Experiments with pure oleic and elaidic acid show that the ozonides (*A* and *B*) are closely similar but nevertheless distinct from one another and that apparently

only one compound is formed in each case. The constitutions (*A*) and (*B*) are assigned. It is therefore impossible that even a



momentary rupture of the acid mols. into diradicals and direct intrusion of the O_3 mol. can occur. Addition of O_3 leads to a very short existence of a primary ozonide and hence to a single C–C linking; during rupture of this linking and establishment of the ether bridge free rotation is possible for an instant but the fixation of substituents occurs at definite places of the C atoms.

The tendency towards the formation of multimol. ozonides is more pronounced with simple than with complex olefines and is very dependent on the solvent, occurring much more readily in CCl_4 than in EtOAc. Polymerisation must occur at the instant when the C–C linking is ruptured; subsequent polymerisation of a monomeride has never been observed but a multimol. compound can become further polymerised. This is indicative of a chain reaction along the lines: $C{:}C + O_2 \rightarrow {:}O{\cdot}O{\cdot}C{\cdot}C{\cdot\cdot} + C{:}C \rightarrow {\cdot\cdot}O{\cdot}O{\cdot}C{\cdot}C{\cdot}C{\cdot}C{\cdot\cdot}$ or

$C{:}C + O_2 \rightarrow {\cdot\cdot}O{\cdot}O{\cdot}C{\cdot}C{\cdot\cdot} + O_2 + C{:}C \rightarrow {\cdot\cdot}O{\cdot}O{\cdot}C{\cdot}C{\cdot}O{\cdot}O{\cdot}C{\cdot}C{\cdot\cdot\cdot}$ etc. or

$C{:}C + O_3 \rightarrow {\cdot\cdot}O{\cdot}O{\cdot}C{\cdot}O{\cdot}C{\cdot\cdot} + O_3 + C{:}C \rightarrow {\cdot}O{\cdot}O{\cdot}C{\cdot}O{\cdot}C{\cdot}O{\cdot}O{\cdot}C{\cdot}O{\cdot}C{\cdot\cdot\cdot}$.

The third type of change could occur through primary ozonides and the rupture of the C·C linking occurs through their transformation. Rupture of the chain can be caused by ring formation; this is probably the case with the multimol. ozonides of the simpler olefines or when a mixture or fission product of the ozonide adds to the reactive terminal positions, thus causing inactivation. Intrusion of ethylenic residues is to be expected, thus involving a polymerisation of the olefine. This does not occur if the concn. of O_3 or O_2 is so high that every radical is immediately trapped. The co-operation of mol. O_2 is to be expected particularly when the concn. of O_3 in the solution is low.

Ozonisation of $(:CHMe)_2$ under the conditions laid down by Harries for the production of the oxozonide and removal of all volatile matter from the product gives a residue similar to Harries' material; a similar product is also obtained by the after-treatment of multimol. butene ozonide with O_3. Physical properties and chemical behaviour towards alkali and $FeSO_4$ show that the product is multimol. ethylidene peroxide, $(C_2H_4O_2)_3$. H. W.

Production of organic peracids and salts thereof.—See B., 1944, II, 219.

Production of lævulic acid [from wood].—See B., 1944, II, 220.

Dehydration of β-hydroxy-βγγ-trimethyl-*n*-valeric acid. M. S. Newman and R. Rosher (*J. Org. Chem.*, 1944, **9**, 221—225).—Dehydration of $OH{\cdot}CMeBu^{\gamma}{\cdot}CH_2{\cdot}CO_2H$ (**I**) and its ester proceeds without mol. rearrangement. $OH{\cdot}CMeBu^{\gamma}{\cdot}CH_2{\cdot}CO_2Me$ (**II**), b.p. 88—90°/14 mm., is obtained in 66% yield by gradually adding a solution of $CH_2Br{\cdot}CO_2Me$ and pinacolone in dry C_6H_6 to Zn foil in presence of a little I. The yield of this or the Et ester (**III**), b.p. 104—107°/18 mm., sinks to ~53% if all the reactants are placed together at once. Treatment of (**II**) with $COCl_2$ and C_5H_5N in Et_2O followed by hydrolysis, heating (**III**) with I followed by hydrolysis, or heating (**I**) with Ac_2O leads to a mixture of a solid acid (**IV**), m.p. 84·5—85·0° (corr.), and a liquid acid (**V**), each of which yields the same *amide*, m.p. 141—142° (corr.); they are regarded as geometrically isomeric forms of *βγγ-trimethyl-Δ$^{\alpha}$-pentenoic acid*. Catalytic reduction (PtO_2) of (**IV**) or (**V**) gives *βγγ*-trimethyl-*n*-valeric [identified as the amide, m.p. 166—167° (corr.)] in 83% yield. (**IV**) or (**V**) is transformed by NaOH at 225° into pinacolone, identified as the 2 : 4-dinitrophenylhydrazone, m.p. 124—125°. Reaction between (**II**) or (**III**) and I is erratic, sometimes giving a lachrymatory liquid, probably iodopinacolone. Al_2O_3 at 300—325° causes cleavage of (**II**). $POCl_3$ in boiling C_6H_6 transforms (**III**) into *β-tert.*-butyl-γ-butyrolactone (**VI**), b.p. 117°/20 mm., m.p. 99—100°, more easily obtained by heating (**I**), (**II**), (**III**), (**IV**), or (**V**) with 50% H_2SO_4 under reflux. (**VI**) is very resistant towards hydrogenation either by HI or in presence of Raney Ni. It is completely degraded by $KMnO_4$ or 50% HNO_3 but untouched by CrO_3. It is readily hydrolysed by alkali, but the liberated acid immediately reverts to (**VI**). With MgPhBr (**VI**) affords (?) 2 : 2-*diphenyl*-4-tert.-*butyltetrahydrofuran*, m.p. 79·5—80·0°. H. W.

Autoxidation of ascorbic acid in presence of copper.—See A., 1944, I, 99.

l-Amino-acid oxidase of *Proteus vulgaris*. P. K. Stumpf and Green (*J. Biol. Chem.*, 1944, **153**, 387—399; cf. A., 1944, III, 888). 2 . 4-*Dinitrophenylhydrazones* of the following are described: 3-indolylpyruvic acid, m.p. 169°, α-ketohexoic acid, m.p. 134°, α-keto-isohexoic acid, m.p. 155°, α-ketovaleric acid, m.p. 160°, 2-iminazolyl pyruvic acid, m.p. 239° (decomp.) [*hydrochloride* (+2H_2O), m.p. 192° (decomp.)], δ-guanido-α-ketovaleric acid, m.p. 267° (decomp.) [*hydrochloride*, (+1H_2O), m.p. 216° (decomp.)]. J. N. A.

Reaction of diazomethane with ammonium salts of organic acids. M. Frankel and E. Katchalski (*J. Amer. Chem. Soc.*, 1944, **66**, 763—765).—NH_4, NH_2Me, NH_2Et, $NHMe_2$, or NEt_3 salts of malonic, succinic, or phthalic acid with CH_2N_2 in Et_2O give 72—92% of the Me_2 ester and the appropriate amine (which is not methylated; cf. A., 1944, II, 15). NH_4Cl and CH_2N_2–Et_2O give NH_3 (69%) and MeCl (53%). R. S. C.

***p*-Carboxyphenylhydrazones of palmit-, m.p. 101—102° (decomp.), and stearaldehyde, m.p. 105° (decomp.), and corresponding carboxymethoximes, m.p. 68—89° and 81—82°, thiosemicarbazones, m.p. 109° and 112°, and glyceryl acetals, m.p. 48—49° and 57° respectively.**—See C., 1944, 117.

Synthesis of hydroxycitronellal.—See B., 1944, II, 220.

Tests of mechanism for the photochemical decomposition of acetone.—See A., 1944, I, 229.

Silver (Ag^{III}) ethylenedibiguanide hydroxide and its salts.—See A., 1944, I, 230.

Peptidases of intestinal mucosa. E. L. Smith and M. Bergmann (*J. Biol. Chem.*, 1944, **153**, 627—651).—The following are preps. of di- and tri-peptides as substrates for the study of peptidase action (cf. A., 1944, III, 689). *l*-Hydroxyproline (**I**), with carbobenzyloxyglycyl chloride (**II**) and 2N-NaOH at room temp. yields *carbobenzyloxyglycyl-l-hyaroxyproline*, m.p. 124—124·5°, hydrogenated (Pd-black) in aq. MeOH–AcOH to glycyl-*l*-hydroxyproline, $[\alpha]_D^6$ −128·4° in H_2O (cf. Abderhalden and Koppel, A., 1928, 1041). (**I**) is esterified by HCl–$CH_2Ph{\cdot}OH$ to *l-hydroxyproline CH_2Ph ester hydrochloride*, m.p. 147—150°, which with carbobenzyloxyglycylglycine azide gives *carbobenzyloxydiglycyl-l-hydroxyproline CH_2Ph ester*, m.p. 123—127°, converted as above into *diglycyl-l-hydroxyproline*, $[\alpha]_D^6$ −97·7° in H_2O. Similarly prepared are *carbobenzyloxydiglycyl-l-proline CH_2Ph ester*, m.p. 87°, and *diglycyl-l-proline*, $[\alpha]_D^{26}$ −101·5° in H_2O. The *Me* ester *hydrochloride* (**III**), m.p. 162—164° (decomp.), of (**I**), coupled with (**II**) and treated with MeOH–NH_3, affords *carbobenzyloxyglycyl-l-hydroxyprolineamide*, m.p. 208°, which on hydrogenation etc. gives *glycyl-l-hydroxyproline diketopiperazine*, $[\alpha]_D^6$ −190·4° in H_2O. Similarly prepared are *carbobenzyloxyglycyl-l-prolineamide*, m.p. 150—151°, and glycyl-*l*-proline diketopiperazine, m.p. 213°, $[\alpha]_D^6$ −197·3° in H_2O (cf. Fischer and Reif, A., 1908, i, 1007). (**III**) with H_2O–$CHCl_3$–MgO, $CH_2Ph{\cdot}O{\cdot}COCl$, and finally C_5H_5N followed by HCl yields *carbobenzyloxy-l-hydroxyproline hydrazide*, m.p. 149—149·5°, from which are prepared in the usual way *carbobenzyloxy-l-hydroxyprolylglycine CH_2Ph ester*, m.p. 153°, and *l-hydroxyprolylglycine*, $[\alpha]_D^{26}$ −22·42° in H_2O. Also prepared are *l-prolineamide hydrochloride*, m.p. 173—175°, and *l-hydroxyprolineamide*, m.p. 139°. F. O. H.

Effect of dielectric constant and temperature on the catalysed decomposition of azodicarbonate ion.—See A., 1944, I, 227.

Interaction of diazomethane with α-cyanocrotonic acid. W. G. Young, L. J. Andrews, S. L. Lindenbaum, and S. J. Cristol (*J. Amer. Chem. Soc.*, 1944, **66**, 810—811).—$CHMe{:}C(CN){\cdot}CO_2H$ (**I**) (modified prep.), m.p. 96—99° (lit. 80°, 92°), with CH_2N_2–Et_2O gives $CMe_2{:}C(CN){\cdot}CO_2Me$ (**II**), m.p. 19·5—21°, b.p. 90—91°/5 mm. [absorption max. at 230 mμ. (ε 11,100) in 95% EtOH], also obtained (m.p. 21·5—22°) by Cope's method (A., 1938, II, 5), but the Ag salt with MeI gives *Me α-cyanocrotonate* (**III**), m.p. 20—22°, b.p. 75·5—76·8°/4—5 mm. [absorption max. at 220 mμ. (ε 8400) in 95% EtOH]. In 3N-NaOH, (**II**) or (**III**) gives $COMe_2$ or MeCHO, respectively, but with O_3 in CH_2Cl_2, (**III**) gives a little MeCHO whereas (**II**) is unaffected. CH_2N_2 converts (**III**) into (**II**). Formation of (**II**) from (**I**) probably occurs by way of (**III**) and the pyrazoline, which is too unstable to exist as such. The mechanism of its formation and decomp. is discussed. R. S. C.

α-Toluenesulphonamido-δ-hydroxyvaleramide, m.p. 182—183° (decomp.).—See A., 1944, III, 605.

Resolution of α-xanthogenopropionic acid into optically active isomerides. A. Fredga and M. Tenow (*Arkiv Kemi, Min., Geol.*, 1943, **17, B**, No. 3, 5 pp.).—(−)-, m.p. 70—71°, $[\alpha]_D^{26}$ −91·1° in EtOAc, −81·8° in EtOH (resolved through the cinchonidine salt, EtOH), and (+)-*xanthogenopropionic acid* (**I**), m.p. 70—70·5°, $[\alpha]_D^{25}$ +92° in EtOAc (*strychnine* salt, +1H_2O), are prepared. (**I**) and conc. NH_3 (1 day), followed by H_2O_2, yield $NH_2{\cdot}CS{\cdot}OEt$ and disulphidodi-α-propionic acid, m.p. 113—115°, $[\alpha]_D^5$ −410° in H_2O. A. T. P.

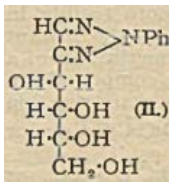
Basically substituted aliphatic nitriles. Their catalytic reduction to [di]amines. F. C. Whitmore, H. S. Mosher, R. R. Adams, R. B. Taylor, E. C. Chapin, C. Weisel, and W. Yanko (*J. Amer. Chem. Soc.*, 1944, **66**, 725—731).—$CH_2{:}CH{\cdot}CN$ (**I**) and NHR_2 yield, by 1 : 4-addition, $NR_2{\cdot}[CH_2]_2{\cdot}CN$ (*A*), the rate of reaction being piperidine > morpholine > $NHEt_2$ and for other $NHAlk_2$ slower as the mol. wt. of R increases; in some cases a catalyst (noted with temp. of prep. below) is needed. The rate is not $\propto k$ of NHR_2. The reaction is reversible, since (i) higher (*A*) dissociate slowly at the

b.p. to give NHR_2; notably (*A*) (R = $[CH_2]_2$·OH) dissociates completely when distilled, (ii) yields are increased by using an excess of either reactant, (iii) hydrogenation (Raney Ni) of (*A*) (NR_2 = morpholino) at 190° gives 35% of morpholine, and (iv) (*A*) (R = H) dissociates when kept into NH_3 and a tarry polymeride of (**I**). NH_2·$[CH_2]_n$·OH and (**I**) in presence of NaOMe give good yields of NR_2·$[CH_2]_n$·O·$[CH_2]_2$·CN. Hal·$[CH_2]_3$·CN and NHR_2 give NR_2·$[CH_2]_3$·CN, yields being much improved by use of a solvent (C_6H_5·$CHCl_3$). Hydrogenation (Raney Ni) of (*A*) at, usually, 90—130°/67—270 atm. gives the diamine with minor amounts of the *sec.* amine (more in the butyro- than in the propio-nitrile series); the amount of *sec.* amine is decreased by presence of an excess of NH_3 and increased by addition of primary amine before hydrogenation. Shaking (**I**) with aq. NH_3 gives mainly $NH([CH_2]_2$·$CN)_2$ (**II**), b.p. 165°/4 mm. (picrate, an oil), and $N([CH_2]_2$·$CN)_3$, but with liquid NH_3 (7 mols.) at ~40° gives NH_2·$[CH_2]_2$·CN (22%), b.p. 66—69°/1 mm. (picrate, m.p. 178°), and (**II**) (64%). The following are described: NR_2·$[CH_2]_2$·CN in which R = Et (best prepared at room temp. and then the b.p.), b.p. 196°/735 mm., 104—106°/35 mm. (picrate, m.p. 85°), Pr^a, b.p. 116°/20 mm. (picrate, m.p. 111°), Bu^a, b.p. 141°/20 mm. (picrate, m.p. 75°), *n*-amyl, b.p. 159—161°/19 mm. (picrate, an oil), and *n*-hexyl, b.p. 145—146°/2 mm. (picrate, an oil); *β-ethylaminopropionitrile* (best at <30° and then 100°), b.p. 92—95°/30 mm. (*picrate*, m.p. 163°); *di-(β-cyanoethyl)ethylamine*, b.p. 200—202°/30 mm. (*picrate*, m.p. 170°); *β-piperidino-*, b.p. 129—130°/30 mm. (*picrate*, m.p. 160°), and β-morpholino-propionitrile, b.p. 149°/20 mm. (picrate, m.p. 139·5°); NR_2·$[CH_2]_3$·CN, in which R = Et, b.p. 101—103°/21 mm. (picrate, m.p. 69—70°), and OH·$[CH_2]_2$ (prep. at room temp.), decomp. when distilled (*picrate*, m.p. 108—109°); γ-piperidino-, b.p. 127—129°/25 mm. (picrate, m.p. 117°), and *γ-morpholino-n-butyronitrile*, b.p. 148—150°/25 mm. (*picrate*, m.p. 152—153°); *β-hydroxy-β′β″-dicyanotriethylamine*, decomp. when distilled (*picrate*, m.p. 137—138°); (CN·$[CH_2]_2$)$_2$O; *NN-diethyl-N′N′-di-β′-cyanoethylpropylene-αγ-diamine*, m.p. 233—235°/25 mm. (*picrate*, m.p. 166—167°); *β-di-(γ′-diethylamino-n-propyl)aminopropionitrile* (at 100°; catalyst: trace of Cu-bronze), b.p. 153°/3 mm. (*picrate*, m.p. 157—158°); *β-β′-morpholinoethyl-*, b.p. 183°/20 mm. (*picrate*, m.p. 176·5°), and *β-γ′-morpholino-n-propyl-*, b.p. 178—180°/9 mm. (*picrate*, m.p. 148—149°), *-aminopropionitrile*; *β-β′-diethylaminoethoxypropionitrile* (prep. at 25°), b.p. 145°/25 mm. (*picrate*, m.p. 75°); *β-γ′-diethylamino-n-propoxypropionitrile*, b.p. 148—150°/25 mm. (picrate, an oil); *β-δ′-diethylamino-α-methyl-n-butoxypropionitrile*, b.p. 125—130°/3 mm. (picrate, an oil); β-N-*methylanilinopropionitrile* (at 180°; catalyst: $CuSO_4$,$5H_2O$; CH_2Ph·NMe_3·OH is ineffective), b.p. 175—177°/29 mm. (*picrate*, m.p. 118°); *9-β-cyanoethylcarbazole* (catalyst: CH_2Ph·NMe_3·OH), m.p. 155·5°; *1-β-cyanoethyl-1 : 2 : 3 : 4-tetrahydroquinoline* (in AcOH at 125°; other catalysts ineffective), b.p. 192°/10 mm. (*picrate*, m.p. 172°); NH_2·$[CH_2]_2$·NR_2 in which R = H, b.p. 138°/735 mm. (picrate, m.p. 178°), Et, b.p. 168°/735 mm. (picrate, m.p. 194°), Pr^a, b.p. 94°/20 mm. (picrate, m.p. 181°), and Bu^a, b.p. 121°/20 mm. (picrate, m.p. 188°); *di-(γ-diethylamino-n-propyl)amine*, b.p. 107°/3 mm. (*picrate*, m.p. 153—154°); *N-ethylpropylene-αγ-diamine*, b.p. 156°/735 mm. (*picrate*, m.p. 193°); γ-piperidino-, b.p. 205°/730 mm. (picrate, m.p. 209—210°), and γ-morpholino-*n*-propylamine, b.p. 219°/733 mm. (picrate, m.p. 166°); *di-(γ-piperidino-*, b.p. 153°/2 mm. (*picrate*, m.p. 193°), and *di-(γ-morpholino-n-propyl)amine*, b.p. 185°/5 mm. (*picrate*, m.p. 213—215°); NR_2·$[CH_2]_4$·NH_2 in which NR_2 = NEt$_2$, b.p. 85—88°/18 mm. (picrate, m.p. 185—186°), piperidino-, b.p. 118—120°/25 mm. (picrate, m.p. 160·5°), and *morpholino-*, b.p. 122°/20 mm. (*picrate*, m.p. 148°); *di-(δ-piperidino-*, b.p. 220—225°/25 mm. (*picrate*, m.p. 202—203°), and *di-(δ-morpholino-n-butyl)amine*, b.p. 200—202°/3 mm. (*picrate*, m.p. 136°); *γ-di-(β′-hydroxyethyl)amino-n-propylamine*, b.p. 158°/2 mm. (*picrate*, m.p. 157—158°); *di-γ-amino-n-propyl ether*, b.p. 113°/32 mm. (picrate, an oil); *γ-γ′-diethylamino-n-propylamino-n-propylamine*, b.p. 142—144°/25 mm.; *di-(γ-γ′-diethylamino-n-propylamino-n-propyl)amine*, b.p. 253—260°/25 mm. (*picrate*, m.p. 197°); *γ-di-(γ′-diethylamino-n-propyl)amino-n-propylamine*, b.p. 155—165°/3 mm. (*picrate*, m.p. 162·5°); *γ-β′-morpholinoethyl-*, b.p. 120—123°/2 mm. (*picrate*, m.p. 208°), and *γ-γ′-morpholino-n-propyl-*, b.p. 137—140°/1·5 mm. (*picrate*, m.p. 205°), *-amino-n-propylamine*; γ-β′-diethylaminoethoxy-, b.p. 118—122°/25 mm. (picrate, an oil), *γ-γ′-diethylamino-n-propoxy-*, b.p. 130—132°/25 mm. (picrate, an oil), *γ-δ′-diethylamino-α-methyl-n-butoxy-*, b.p. 80—83°/2 mm. (*picrate*, m.p. 88—89°), and γ-N-*methylanilino-*, b.p. 171—172°/40 mm. (*picrate*, m.p. 189°; *hydrobromide*, m.p. 120°), -n-*propylamine*; *di-(γ-β′-diethylaminoethoxy-*, b.p. 175°/3 mm. (picrate, an oil), *di-(γ-γ′-diethylamino-n-propoxy-*, b.p. 182°/3 mm. (picrate, an oil), and *di-(γ-δ′-diethylamino-α-methyl-n-butoxy-*, b.p. 210—215°/3 mm. (picrate, an oil), -n-*propyl)amine*; *9-γ-amino-n-propylcarbazole*, cryst., b.p. 228°/3 mm. (*picrate*, m.p. 206—207°; *hydrochloride*, m.p. 273°); *1-γ-amino-n-propyl-1 : 2 : 3 : 4-tetrahydroquinoline*, b.p. 132—135°/3 mm. *β-γ′-Diethylamino-n-propylamino-n-propionitrile*, b.p. 163—165°/2 mm. (picrate, m.p. 123°), is prepared from NEt_2·$[CH_2]_3$·NH_2 by (**I**) or Br·$[CH_2]_2$·CN, thereby proving the structure of the products. The appropriate diamine with *p*-NHAc·C_6H_4·SO_2Cl–K_2CO_3–$COMe_2$–H_2O and then 20% HCl yields N^1-*γ-diethylamino-*, m.p. 109—110°, *-di-n-propylamino-*, m.p. 98—98·5°, -di-*n*-butylamino-(*hydrochloride*, m.p. 110—115°), *-piperidino-*, m.p. 105·5—106° (*Ac* derivative, m.p. 109—111°), and *-morpholino-*, m.p. 94·5—95° (*Ac* derivative, m.p. 97—98°), -n-*propylsulphanilamide*, *N^{1}N^1*-di-(γ-diethylamino-*n*-propyl)- (*hydrochloride*, m.p. 195—197°; *Ac* derivative, m.p. 83—85°), and N^{1}N^1-*di-(γ-piperidino*-n-*propyl)-sulphanilamide*, m.p. 171°. R. S. C.

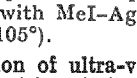
Action of ammonia on allophanic azide. W. L. Lipschitz (*J. Amer. Chem. Soc.*, 1944, **66**, 658).—Contrary to Thiele *et al.* (A., 1899, i, 118), allophanic azide with conc. aq., dil. aq., or liquid NH_3 gives only biuret. R. S. C.

II.—SUGARS AND GLUCOSIDES.

Action of copper sulphate on phenylosazones of sugars. Phenyl-*D*-glucosotriazole. R. M. Hann and C. S. Hudson (*J. Amer. Chem. Soc.*, 1944, **66**, 735—738).—Phenyl-*D*-glucosazone (**I**) (5 g.) and $CuSO_4$ (2 mols.) in boiling H_2O give *2-phenyl-D-glucosotriazole* (**II**) (2—3 g.), m.p. 195—196°, $[\alpha]_D^{20}$ −81·6° in C_5H_5N (*tetra-acetate*, m.p. 81—82°, $[\alpha]_D^{20}$ −25·6° in $CHCl_3$; *tetrabenzoate*, m.p. 112—113°, $[\alpha]_D$ +3·0° in $CHCl_3$), and NH_2Ph (20% isolated as NHPhAc) (cf. A., 1934, 633). Triazoles are similarly obtained (no details given) from the phenylosazones of *L*-sorbose (50%; m.p. 158—159°), *D*-galactose (**III**) (47%; m.p. 110—111°), *D*-altrose (62%; m.p. 134—135°), *D*-xylose (40%; m.p. 88—90°), cellobiose (62%; m.p. 164—165°), lactose (**IV**) [62%; (**V**), m.p. 180—181°], and turanose (**VI**) (70%; m.p. 193—194°). The reaction occurs in two stages, evident with the sol. phenylosazones of (**IV**) and (**VI**); a red Cu–osazone complex first forms and then decomposes to the colourless triazole, leaving the solution green owing to the Cu–NH_2Ph colour. (**V**) is hydrolysed by acids as readily as is (**IV**) and yields (**II**) and (**III**). (**I**) is readily identified by this reaction in acidified aq. Pr$^\beta$OH (cf. C., 1944, Part 4). R. S. C.



(III)

Acyclic sugar orthoacetate. M. L. Wolfrom and D. I. Weisblat (*J. Amer. Chem. Soc.*, 1944, **66**, 805—806).—Crude 1-chloro-1-ethylthiol-*aldehydo-D*-galactose penta-acetate, m.p. 95—98° (A., 1941, II, 211), with $CaSO_4$ and Ag_2CO_3 in EtOH at room temp. gives *D*-galactose Et_2 monothioacetal penta-acetate (A., 1940, II, 205) and a small amount of *1-ethylthio*aldehydo-D-*galactose Et* 1 : 2-*orthoacetate tetra-acetate*, 

{R = [CH(OAc)]$_3$·CH_2·OAc}, m.p. 125—126°, $[\alpha]_D^{24}$ +54° in $CHCl_3$, from which 5 Ac are removed by acid but only the 4 normal Ac by alkali. R. S. C.

Methyl-3-methyl-4 : 6-ethylidene-β-glucosides. R. E. Reeves (*J. Amer. Chem. Soc.*, 1944, **66**, 845).—Mixed methyl-3-methyl-α- and -β-glucosides (from the syrupy triacetate) with paraldehyde and a little conc. H_2SO_4 at room temp. give *methyl-3-methyl-4 : 6-ethylidene-α-*, m.p. 106—107° (corr.), $[\alpha]_D^{25}$ +114°, $[\alpha]_{Hg\ blue}^{25}$ +246° in H_2O, and *-β-glucoside*, m.p. 133—134° (corr.), $[\alpha]_D^{25}$ −66°, $[\alpha]_{Hg\ blue}^{25}$ −126° in H_2O (with MeI–Ag_2O gives the known 2 : 3-Me_2 compound, m.p. 103—105°). R. S. C.

Action of ultra-violet light on cellulose. I. Irradiation effects. II. Post-irradiation effects. R. A. Stillings and R. J. van Nostrand (*J. Amer. Chem. Soc.*, 1944, **66**, 753—760).—The photolysis of cellulose (**I**) in O_2 and in N_2 has been studied (for apparatus see C., 1944, Part 4). Glucose and cellobiose (**II**) have been irradiated in N_2. (**I**) in N_2 is considerably degraded (lowering of degree of polymerisation and α-cellulose content, increase in Cu no., and liberation of CO and CO_2), the degradation increasing with time of exposure. These changes are not related to the presence of O_2 in the N_2 or in the (**I**). Rate of degradation increases with increasing O_2 in the gas phase, but rate of change of chain length and Cu no. do not correspond with a first-order reaction. β-*d*-Glucose and (**II**) liberate CO and CO_2, but more slowly than (**I**). If (**I**) which has been irradiated in the absence of O_2 is left in air the changes brought about by irradiation continue to occur but cease when air is absent. Post-irradiation effects are enhanced by increased temp. to 70° and also by O_2 instead of air, but diminished by replacement of O_2 by N_2. Reintroduction of O_2 causes production of post-irradiation effects. For (**I**) irradiated in O_2 the post-irradiation effects are less marked and of shorter duration. W. R. A.

III.—HOMOCYCLIC.

Thermal decomposition of substituted *cyclo*hexenes. F. O. Rice and M. T. Murphy (*J. Amer. Chem. Soc.*, 1944, **66**, 765—767).—On pyrolysis at ~700° 1-methyl-, 3-vinyl-, and 1-phenyl-*cyclo*hexene yield the expected substituted butadiene and C_2H_4. Ethyl*cyclo*hexene does not yield the expected ethylbutadiene. Dipentene gives a high yield of isoprene, but 3-*p*-menthene does not give *iso*propylbutadiene although it gives a high yield of CH_2:CHMe. W. R. A.

Debromination of pentaerythrityl bromide by zinc. Isolation of *spiro*pentane. M. J. Murray and E. H. Stevenson (*J. Amer. Chem. Soc.*, 1944, **66**, 812—816).—A detailed account of work already

reported (A., 1944, II, 215). Raman spectra are recorded for *spiro*pentane, methylene- and methyl-*cyclo*butane, and *cyclo*butanone. R. S. C.

Friedel–Crafts synthesis of ketones and hydrocarbons by means of aluminium chloride and gallium chloride. H. Ulich (*Oel u. Kohle*, 1943, **39**, 523—527).—The ketone synthesis takes place either as a homogeneous reaction after $AlCl_3$ has gone into solution in the form of an additive complex or as a surface reaction if excess of solid $AlCl_3$ is present. The hydrocarbon synthesis is autocatalytic and proceeds rapidly after a heavy oily phase has been formed by addition of $AlCl_3$ to the reaction products. Addition of C_2H_4 to C_6H_6 proceeds by formation of EtCl if HCl is present, but direct addition by a surface reaction on $AlCl_3$ is possible. Since $GaCl_3$ is readily sol. in C_6H_6 the hydrocarbon synthesis with $GaCl_3$ is a purely homogeneous reaction. Addition of C_2H_4 to C_6H_6 is direct and not accelerated by HCl. PhEt is the main reaction product. R. B. C.

Esters of *p*-toluenesulphonic acid. R. S. Tipson (*J. Org. Chem.*, 1944, **9**, 235—241).—Esters of *p*-$C_6H_4Me{\cdot}SO_3H$ are obtained usually in >75% yield by the action of *p*-$C_6H_4Me{\cdot}SO_2Cl$ on the requisite alcohol or phenol in dry C_5H_5N which must be shielded from atm. moisture. Generally, but not always, the temp. of the reacting mixture should be ≯0°. Nothing is gained in small experiments by addition of the reactants in portions. Technical *p*-$C_6H_4Me{\cdot}SO_2Cl$ suffices, an excess of ~10% being used. Under these conditions chlorination is never observed even with $OPh{\cdot}[CH_2]_2{\cdot}OH$ or 2 : 4 : 1-$(NO_2)_2C_6H_3{\cdot}OH$, which readily yield Cl-compounds with *p*-$C_6H_4Me{\cdot}SO_2Cl$ in warm (or hot) C_5H_5N or $NPhEt_2$. The tendency towards the production of pyridinium salts, usually pronounced with EtOH, $CH_2Ph{\cdot}OH$, and 2 : 4 : 1-$(NO_2)_2C_6H_3{\cdot}OH$, is overcome by neutralising the excess of C_5H_5N as soon as esterification is considered to be complete. *β-Methoxyethyl*, b.p. 141°/0·2 mm., m.p. 10°, *-ethoxyethyl*, b.p. 122°/0·1 mm., m.p. 18·5°, *-n-propoxyethyl*, b.p. 140°/0·1 mm., m.p. 8°, *-n-butoxyethyl*, b.p. 142°/0·1 mm., *-phenoxyethyl*, m.p. 80—81°, and *diethylcarbinyl*, m.p. 43—44°, *p-toluenesulphonate* are new. *apo*Cupreine gives a *mono*-p-*toluenesulphonate*, amorphous, $[\alpha]_D^{24}$ +14·8° in abs. EtOH. H. W.

Interaction of benzene with butadiene in presence of sulphuric acid and hydrogen fluoride catalysts. V. N. Ipatiev, H. Pines, and R. E. Schaad (*J. Amer. Chem. Soc.*, 1944, **66**, 816—817).—The low-boiling fraction obtained from $(CH_2{:}CH)_2$ and an excess of C_6H_6 in H_2SO_4 at 0—5° (14% yield) or HF at 5—20° (59% yield) is $CHPhEt{\cdot}CH_2Ph$, b.p. 148°/12 mm. (NHAc-derivative, m.p. 219°), also obtained [b.p. 141°/12 mm. (*NHAc*-derivative, m.p. 227°), from $CH_2Ph{\cdot}COPh$ by interaction with MgEtBr, followed by dehydration over activated Al_2O_3 at 350°, and hydrogenation (Raney Ni; C_6H_{12}; 50°/100 atm.). $COPh_2$ and $MgPr^{\alpha}Br$ etc. lead to $CHPh_2Pr^{\alpha}$, b.p. 145°/16 mm. (*NHAc*-derivative, m.p. 201—203°). COPhMe and $MgBr{\cdot}[CH_2]_2{\cdot}Ph$ etc. lead to $CHPhMe{\cdot}[CH_2]_2{\cdot}Ph$, b.p. 291° (*NHAc*-derivative, m.p. 194°). R. S. C.

Pyrolysis of [asymmetric] diphenylethane compounds.—See B., 1944, II, 221.

Mechanism of peroxide-initiated styrene polymerisation.—See A., 1944, I, 227.

Morphine-like properties of [αβ-]diphenylethylamine and related compounds. E. C. Dodds, W. Lawson, and P. C. Williams (*Proc. Roy. Soc.*, 1944, **B**, **132**, 119—132; see also A., 1944, III, 683).—The following are obtained by reduction (Na–Hg, EtOH–AcOH) of the appropriate ketoxime: *αβ-di-p-anisylethylamine*, m.p. 103—104° (hydrochloride, m.p. 210—212°); *β*-phenyl-*α*-*p*-anisyl-, an oil (*hydrochloride*, m.p. 215—217°), demethylated by HI (*d* 1·7) to *β*-phenyl-*α*-*p*-hydroxyphenyl-ethylamine (*hydrochloride*, m.p. 194—195°); *β*-cyclo*hexyl-α-phenylethylamine*, b.p. 162—164°/12 mm. (*Bz* derivative, m.p. 168°; picrate, m.p. 183—184°; hydrochloride, m.p. 280—282°); *β*-cyclo*hexyl-α-p-anisylethylamine*, b.p. 130—135°/0·2 mm. (hydrochloride, m.p. 246—248°). $COPh{\cdot}CHPh{\cdot}NH_2$,HCl and MgEtI (6 mols.) give *β*-hydroxy-*αβ*-diphenyl-*n*-butylamine, an oil (*hydrochloride*, m.p. 215—217°); *β*-hydroxy-*αβ*-diphenyl-*n*-propyl- (*hydrochloride*, m.p. 248—250°) and -n-butyl-dimethylamine (*hydrochloride*, m.p. 251—252°) are similarly obtained from $COPh{\cdot}CHPh{\cdot}NMe_2$,HCl and MgAlkI. *Ph hexahydrobenzyl ketone*, b.p. 169—170°/12 mm. (2 : 4-dinitrophenylhydrazone, m.p. 157—158°; oxime, m.p. 100—101°), is prepared from *cyclo*hexylacetyl chloride, C_6H_6, and $AlCl_3$. H. B.

***p*-Dimethylamino-derivatives of nitrostyrene.** D. E. Worrall and Cohen (*J. Amer. Chem. Soc.*, 1944, **66**, 842).—*p*-$NMe_2{\cdot}C_6H_4{\cdot}CHO$ with $MeNO_2$ or $EtNO_3$ and a little n-$C_5H_{11}{\cdot}NH_2$ at 100° gives *β-nitro*-p-*dimethylaminostyrene* (I), m.p. 179—180·5°, and *β-nitro-α*-p-*dimethylamino-*Δ^{α}*-propene*, m.p. 118—120°, respectively. With $NHPh{\cdot}NH_2$ (excess), (I) gives *p*-$NMe_2{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}NHPh$ and with Br–$CHCl_3$ first at the b.p. and then in sunlight gives *α-bromo-β-nitro*-p-*dimethylaminostyrene*, m.p. 121°. R. S. C.

***o*-Diphenylyl- and 2-di*cyclo*hexylyl-carbimide, *s*-di-*o*-diphenylyl- and *s*-di-2-di*cyclo*hexylyl-carbamide.** H. Fraenkel-Conrat and H. S. Olcott (*J. Amer. Chem. Soc.*, 1944, **66**, 845).—The appropriate amine and $COCl_2$ in boiling PhMe give o-*diphenylyl-*, b.p. 100°/0·5—1 mm., and 2-*dicyclohexylyl-carbimide*, b.p. 89—90°/0·5—1 mm., converted by aq. C_5H_5N at room temp. and 100°, respectively, into *s-bis-o-diphenylyl-*, m.p. 182°, and *s-bis-2-dicyclohexylyl-carbamide*, m.p. 225—228°. R. S. C.

Derivatives of sulphanilamide.—See B., 1944, III, 186.

***p*-Aminobenzenesulphonacylamides.**—See B., 1944, III, 167.

Orientation in the diphenyl series. (A) Preparation of 2- and 4-aminodiphenyl-4′-sulphonamides. A. H. Popkin and G. B. McVea. **(B) Derivatives of 2-aminodiphenyl.** A. H. Popkin, G. M. Perretta, and R. Selig (*J. Amer. Chem. Soc.*, 1944, **66**, 796—798, 833—834).—(A) NHAc, NH_2,HCl, or NH_2 attached to Ph_2 acts in acid as a *m*-orienting group, directing substituents to $C_{(4')}$. *o*- or *p*-$C_6H_4Ph{\cdot}NH_2$,HCl in $ClSO_3H$ at 10° and later 60° give, after treatment with NH_3, 2- and 4-$NH_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$-4′, respectively. The same products are obtained from the free amines, which, however, are less reactive than their salts, requiring temp. up to 90° for sulphonation.

(B) *o*-$C_6H_4Ph{\cdot}NH_2$ with Me_2SO_4–30% NaOH at <30° gives 92% of a 66 : 34 mixture of *o*-$C_6H_4Ph{\cdot}NMe_2$ (I), b.p. 115—116°/2—3 mm., and *o*-$C_6H_4Ph{\cdot}NHMe$ (II) [isolated as *Ac* derivative (III), m.p. 98—99°] (cf. Evans *et al.*, A., 1939, II, 414), and with MeOH–H_2SO_4 gives an 87 : 13 mixture of (I) and (II). The structure of (III) is proved by synthesis from *o*-$C_6H_4Ph{\cdot}NHAc$ (IV) by Na, followed by MeI, in hot xylene. (III) is less readily hydrolysed by MeOH–conc. aq. HCl than is (IV). $CuSO_4$, PhOH, and aq. NaCl convert (I) into an analogue of methyl-violet. R. S. C.

Synthesis of 1 : 2-diamino*cyclo*butane. Z. I. Schuikina (*J. Gen. Chem. Russ.*, 1943, **13**, 373—381).—For the purpose of studying its behaviour towards oxidising agents, 1 : 2-diamino*cyclo*butane was prepared. $(CH_3{\cdot}CHBr{\cdot}CO_2Et)_2$ (Stephen *et al.*, *J.C.S.*, 1913, **103**, 271) with NaCN (Fuson *et al.*, A., 1929, 794) gives Et_2 1-cyano*cyclo*butane-1 : 2-dicarboxylate, hydrolysed [$Ba(OH)_2$] to *cyclo*butane-1 : 1 : 2-tricarboxylic acid, which is decarboxylated at 150° to mixed *cis*- and *trans-cyclo*butane-1 : 2-dicarboxylic acids, and the mixture is then treated with conc. aq. HCl at 190°/4 hr. to give wholly the *trans*-form. The derived Me_2 ester (MeOH–HCl or –H_2SO_4) with NH_3 gives the diamide, which with KOBr affords 1 : 2-*diamino*cyclo*butane* (I) [*hydrochloride* (II), decomp. 240° without melting; *platinichloride*; *picrate* +1H_2O, resinifies at >200°]. Treatment of (II) with solid KOH and then with fused BaO gives a mixture of (I) and pyrrole (?). F. Hi.

Diazoamino-compounds.—See B., 1944, III, 186.

Action of aluminium chloride on phenyl ethers. G. Baddeley (*J.C.S.*, 1944, 330—332).—Alkylation of the PhOH nucleus is solely *para*- in presence of $AlCl_3$, whereas that of homologues is directed by alkyl in the nucleus. Ethylation occurs more readily than methylation and the products readily isomerise. PhOMe and $AlCl_3$ (1 mol.) give a complex, $PhO(Me){\cdot}AlCl_3$, which decomposes at >40° to $PhO{\cdot}AlCl_2$ and MeCl, and at 100° for 2 hr. affords PhOH (I) in quant. yield. With 2 mols of $AlCl_3$, the products formed from PhOMe at 100°/1 hr. are (I) (68%), *p*-cresol (II) (16%), *o*-4-xylenol (III) (8%), and hemimellithenol (IV) (5%). The methylating agent is probably $MeCl,AlCl_3$, and no *o*-cresol is formed. Similarly, (I), Et_2O, and $AlCl_3$ (2·8 mols.) at 100° for 3 hr. give 15% of *p*-$C_6H_4Et{\cdot}OH$ but no *o*-isomeride. *p*-$C_6H_4Me{\cdot}OMe$ (V) and 0·5, 1·25, or 2 mols. of $AlCl_3$ at 100° for 2·75, 3, or 1 hr. give 50% of (V) + 50% of (II), 40% of (II) + 40% of (III) + 10% of (IV), or 30% of (II) + 40% of (III) + 20% of (IV) + a substance (VI), m.p. 125° (probably $C_6Me_5{\cdot}OH$), respectively. With $AlCl_3$ (1·1 mols.) at 100°, PhOMe affords (I) (95%), *m*-$C_6H_4Me{\cdot}OMe$ gives *m*-cresol (80%) and (III) (15%), whilst 1 : 3 : 5-$C_6H_3Me_2{\cdot}OMe$ gives *m*-5-xylenol (70%), (IV) (20%), and higher homologues containing (VI). *o*-$C_6H_4Me{\cdot}OMe$ and $AlCl_3$ similarly yield *o*-cresol, *p*- (38%) and *o*-3-xylenol, and *iso-ψ*-cumenol (24%), m.p. 95°. *p*-$C_6H_4Me{\cdot}OEt$ and $AlCl_3$ (2 mols.) at 100° for 10 min. give (II), 1 : 2 : 4-$C_6H_3MeEt{\cdot}OH$ (VII) (27%), and 2 : 6-*diethyl*-p-*cresol* (VIII) (18%), m.p. 59° (also obtained by Clemmensen reduction of 4 : 2 : 6 : 1-$OH{\cdot}C_6H_2Et_2{\cdot}CHO$). (II), EtBr, and $AlCl_3$ at 20° for 3 days afford 26% of (VII) and 31% of (VIII). *p*-$C_6H_4Et{\cdot}OH$ and MeBr similarly give some 1 : 6 : 3-$C_6H_3MeEt{\cdot}OH$. A mixture of equal amounts of *m*- and *p*-$C_6H_4Me{\cdot}OMe$ at 125—130° yields (III) and *m*- (54%) + *p*-cresol (46%); interconversion of these cresols is not appreciable and thus methylation of *p*-$C_6H_4Me{\cdot}O{\cdot}AlCl_2$ is at least as ready as that of the *m*-isomeride. (II) and $AlCl_3$ (5 mols.) in Et_2O at 75—80° for 4 hr. or 100° for 1 hr. give (VII) (9 or 18%), whereas at 80° for 48 hr. or 100° for 3·5 hr., 1 : 5 : 3-$C_6H_3MeEt{\cdot}OH$ (IX) (45 or 40%) is formed, probably by isomerisation of (VII). Similarly, ethylation of *m*-cresol at 100° for 30 hr. gives 38% of (IX), probably formed from the 6-isomeride. Ethylated cresols are accompanied by an alkali-insol. substance, b.p. 138°/20 mm. Alkylation occurs in the *o*-position to $\cdot O{\cdot}AlCl_2$ only when the *p*- and both *m*-positions are occupied by alk. Products are identified by mixed m.p., directly or of their *p*-nitrobenzoates. p-*Nitrobenzoates* (m.p. in parentheses) of the following phenols are prepared: PhOH (129°); *o*- (94°), *m*- (87°), and *p*-cresol (100°); *o*-3- (104·5°), *o*-4- (128°), *m*-2- (99°), *m*-4- (113°), *m*-5- (109°), and *p*-xylenol (88°); *o*- (57°), *m*- (68°), and

o-C_6H_4Et·OH (80°); 4- (88°), 5- (84°), and 6-ethyl-*m*-cresol (116°); 2- (116°) and 3-ethyl-*p*-cresol (98°); hemimellithenol (147°). A. T. P.

β-*p*- and β-*o*-Anisylpropylmethylamines.—See B., 1944, II, 248.

Dimerisation of 6-methoxy-3 : 4-dihydronaphthalene. R. B. Woodward and R. H. Eastman (*J. Amer. Chem. Soc.*, 1944, **66**, 674—679).—6-Methoxy-1 : 2 : 3 : 4-tetrahydronaphthalene (**I**) and Pb_3O_4 in Ac_2O–AcOH yield 1-*aceloxy*-6-*methoxy*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (**II**), b.p. 144—149°/3 mm. Hydrogenation of 1-keto-6-methoxy-1 : 2 : 3 : 4-tetrahydronaphthalene (**III**) [absorption max. at 276 mμ. (log ε 4·22)] is erratic, yielding (**I**) or 1-hydroxy-6-methoxy-1 : 2 : 3 : 4-tetrahydronaphthalene (**IV**), b.p. 175°/16 mm. Contrary to Long *et al.* (A., 1942, II, 96), 46% HBr converts (**II**) or (**IV**) into 6 : 6′-*dimethoxy*-1 : 2 : 3 : 4 : 3′ : 4′-*hexahydro*-1 : 2′-*dinaphthyl* (**V**), m.p. 76—77° [absorption max. at 274 mμ. (log ε 4·25)], purified by chromatography (Al_2O_3), the dimeric nature of which is proved by its mol. wt. (Rast) and consumption of 1 BzO_2H to give the 1′ : 2′-*oxide*, m.p. 127—128·5° [absorption max. at 283 mμ. (log ε 3·54)]. Hydrogenation of (**V**) gives an oily H_8-derivative, which in boiling 57% aq. HI–AcOH gives 6 : 6′-*dimethoxy*-1 : 2 : 3 : 4 : 1′ : 2′ : 3′ : 4′-*octahydro*-1 : 2′-*dinaphthyl*, mixed stereoisomerides, m.p. up to 187—190°; demethylation of (**V**) is anomalous. $KMnO_4$–$NaHCO_3$ oxidises (**V**) at 0° to give small yields of β-2-*carboxy*-5-*methoxyphenylpropionic acid*, m.p. 201·5—203°, and 6 : 6′-*dimethoxy*-1 : 2 : 3 : 4-*tetrahydro*-1 : 2′-*dinaphthyl* (**VI**), m.p. 107·5—108·5°, but CrO_3–AcOH gives only a little (**VI**). With 10% Pd–C in CO_2 at 300° (or, less well, S at 200—300°), (**V**) gives 6 : 6′-*dimethoxy*-1 : 2′-*dinaphthyl* (**VII**), m.p. 91—92°, converted by 57% HI–AcOH into 6 : 6′-*dihydroxy*-1 : 2′-*dinaphthyl*, m.p. 187—188·5°. Freshly distilled 2 : 6-$C_{10}H_6$Br·OMe (prep. from the naphthol by MeOH–H_2SO_4), m.p. 105—106°, b.p. 160—164°/3 mm., with Mg and a little I in Et_2O and then boiling C_6H_6 gives the Grignard reagent, which with (**III**) gives 6 : 6′-*dimethoxy*-3 : 4-*dihydro*-1 : 2′-*dinaphthyl*, m.p. 126°, and thence by Pd–C at 300° yields (**VII**) or by H_2–PtO_2 in AcOH gives (**VI**). Distillation of crude (**IV**) sometimes gives 7-*methoxy*-1 : 2-*dihydronaphthalene*, b.p. 107—111°/2·5 mm. [absorption max. at ~270 mμ. (log ε ~4·0)], converted by 46% HBr into (**V**). R. S. C.

α-Chloro-αββ-tri-*p*-anisylethylene.—See B., 1944, II, 248.

Constitution of compounds of the type R_nSX_n, R_nSeX_n, and R_2TeX_n.—See A., 1944, I, 192.

Substituted sulphanilamidophenols.—See B., 1944, III, 168.

Water-soluble derivatives of 4 : 4′-diaminodiphenyl sulphone.—See B., 1944, III, 185.

Specificity of the action of *i*-inositol, growth factor of micro-organisms.—See A., 1944, III, 615.

αγ : βδ-Dibenzylidene-*D*-sorbitol.—See A., 1944, II, 286.

Preparation of β-amino-α-3 : 4-dihydroxyphenylbutan-α-ol. C. M. Suter and A. W. Ruddy (*J. Amer. Chem. Soc.*, 1944, **66**, 747—748).—*o*-$C_6H_4(OH)_2$ and $Pr^{\alpha}COCl$ in PhCl at 50°, followed by $AlCl_3$ first in the cold and then at 110°, give 3 : 4 : 1-$(OH)_2C_6H_3$·$COPr^{\alpha}$ (**I**) (68%), m.p. 146—146·5°, the $(CH_2Ph)_2$ ether (**II**), m.p. 86—87°, of which yields with Br–$CaCO_3$ in CH_2Cl_2 α-*bromo*-3 : 4-*dibenzyloxybutyrophenone*, m.p. 100—101°. This does not react smoothly with NH_3 or $(CH_2)_6N_4$ but with $CHPh_2$·NH_2 in boiling EtOH etc. gives α-*benzhydrylamino*-3 : 4-*dibenzyloxy*-n-*butyrophenone hydrochloride* (75%), m.p. 175—176° (decomp.), converted by H_2–Pd-sponge in EtOH at 55—70°/50 lb. into β-*amino*-α-3 : 4-*dihydroxyphenyl*-n-*butan*-α-*ol hydrochloride*, m.p. 199—200° (decomp.). R. S. C.

Preparation of iodine-containing *X*-ray contrast substances. IV. Ethyl iodophenylundecoate ("pantopaque"). W. Baker, E. E. Cook, and (in part) W. G. Leeds (*J.S.C.I.*, 1944, **63**, 223—224; cf. A., 1944, II, 24).—A detailed process is described for the prep. of Et iodophenylundecoate, an *X*-ray contrast substance for the visualisation of the spinal canal and other body cavities. Undecenoic acid and C_6H_6 are condensed to give phenylundecoic acid, which is directly iodinated in AcOH solution in presence of HIO_3, and the product esterified. The overall yield of purified material is 70%.

Effect of substituents on dissociation constants of carboxylic acids.—See A., 1944, I, 224.

Rearrangement of 5-bromosalicylic acid and its ethers by hydrolysis of the bromomagnesium salts. M. Paty and R. Quelet (*Compt. rend.*, 1943, **217**, 229—231).—2 : 5 : 1-OMe·C_6H_2Br·CO_2MgBr (**I**) (from the acid and MgEtBr) is converted by dil. HCl into 4 : 3 : 1-OMe·C_6H_3Br·CO_2H. 4 : 3 : 1-OH·C_6H_3Br·CO_2H is similarly produced starting from 2 : 5 : 1-OH·C_6H_3Br·CO_2H. No rearrangement occurs when, *e.g.*, (**I**) is decomposed by Et_2O–HCl. It is not certain that H_2O is solely responsible for the rearrangement. It is possible that similar rearrangement occurs during decomp. of the carbonation products of the Mg derivatives of 2 : 4-dihalogenoanisoles (*ibid.*, 1942, **214**, 910). F. R. S.

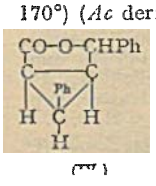
Amines related to epinephrine. I. Amines of the "eprocaine" type. R. Hill and G. Powell (*J. Amer. Chem. Soc.*, 1944, **66**, 742—743).—3 : 4 : 1-$(OH)_2C_6H_3$·CO·CH_2Cl and *p*-NH_2·C_6H_4·CO_2R in boiling H_2O give *Et* (**I**), m.p. 220—221° (darkens) (lit. 201°) [*triacetate* (**II**), m.p. 143—144°], Pr^{α}, m.p. 210—211° (*triacetate*, m.p. 129—131°, Bu^{α}, m.p. 196—196·5° (*triacetate*, m.p. 120°), β-diethylaminoethyl (**III**) [hydrochloride, m.p. ~205° (darkens)], β-di-*n*- (**IV**) (*hydrochloride*, m.p. 223—224°), and -*iso*-propylaminoethyl [*hydrochloride*, m.p. ~225° (darkens)], and β-di-*n*-butylaminoethyl (*hydrochloride*, m.p. 227—230°) *p*-3′ : 4′-dihydroxyphenacylaminobenzoate. Ac_2O–20% NaOH converts (**I**) into a *diacetate*, m.p. 179—181°; (**II**) etc. are prepared by warm Ac_2O–H_2SO_4. 0·1N-NaOH hydrolyses (**IV**) to p-3′ : 4′-*dihydroxyphenacylaminobenzoic acid*, decomp. 241° (bath preheated at 230°). (**III**) [= Eprocaine] has pressor as well as anæsthetic activity (cf. Osborne, *Science*, 1935, **85**, 105), though it causes tissue damage, but the simple alkyl esters have no anæsthetic action. R. S. C.

***N*-Hydroxy-α-amino-acids as possible intermediates in the oxidative degradation of α-amino-acids.** R. E. Steiger (*J. Biol. Chem.*, 1944 **153**, 691—692).—*N*-Hydroxy-*dl*-β-phenylalanine, m.p. 164—165 (corr.; decomp.), rapidly *N*-acetylated and converted into the azlactone, which is dissolved in boiling 67% AcOH to open the ring, yields α-acetamidocinnamic acid, converted into phenylpyruvic acid by boiling with N-HCl. This demonstrates the possibility of converting an *N*-hydroxy-α-amino-acid into an α-keto-acid through the α-imino-acid. J. F. M.

Alkaline fading of tetraiodophenolsulphonephthalein.—See A., 1944, I, 211.

Semi-nitrile of α-hydroxy-β-phenyl-α-benzylsuccinic acid. P. Cordier and J. Moreau (*Compt. rend.*, 1943, **217**, 199—201).—Condensation of CH_2Ph·CN with CH_2Ph·CO·CO_2H in 3% KOH gives 22% of a mixture of the stereoisomerides, m.p. 200° (**I**) (18%) and 158° (**II**) (4%), of CN·CHPh·C(OH)(CH_2Ph)·CO_2H (cf. A., 1935, 975). HCl–AcOH with (**II**) affords the corresponding *imide*, m.p. 161°, with a trace of α-phenyl-β-benzylmalcic anhydride (cf. *loc. cit.*). Conc. H_2SO_4 with (**I**) yields a mixture of the corresponding *amide*, m.p. 210°, and CH_2Ph·CO·CHPh·CO·NH_2, m.p. 165°. F. R. S.

Truxillic acids. I. Rearrangement of ζ-truxinamic acids. General theory of molecular rearrangements. I. S. Goldstein and H. I. Bernstein (*J. Amer. Chem. Soc.*, 1944, **66**, 760—763).—*p*-Truxinic acid and fused KOH give δ- and thence (169 g.), by NaOAc (145) and Ac_2O (365 g.) at 200—210°, ζ-truxinic acid (**I**). The anhydride (prep. by Ac_2O) of (**I**) with NH_3–C_6H_6 gives ζ-truxinic-α-amide acid, which with 0·5N-NaOCl at 38—40° gives ζ-truxinic-α-amino-acid (**II**), m.p. 178—180° (decomp.; bath preheated at 170°) (*Ac* derivative, m.p. 224—225°). With NH_3–EtOH, (**I**) gives



(**III**)

the NH. salt, which at 200—210° yields the imide, converted by 10% KOH–EtOH into the *b*-amide-acid, m.p. 229—230° (decomp.; bath preheated at 220°), and thence, as above, the *b*-amino-acid (**III**), m.p. 171—173° (*Ac* derivative, m.p. 124—125°). With NOBr–Et_2O at −5° or aq. HNO_2 at 40°, (**II**) gives the lactone (**IV**), m.p. 133° (cf. Schenck, A., 1932, 1029). NOBr converts (**III**) into a Br-acid, m.p. 137—139°, and HNO_2 gives an oil with traces of a substance, m.p. 188—189°. These results do not accord with theory (A., 1942, II, 312). R. S. C.

Synthesis of β-bromoethylphthalimide. T. O. Soine (*J. Amer. Pharm. Assoc.*, 1944, **33**, 141—142).—*o*-$C_6H_4(CO)_2N$·$[CH_2]_2$·OH (from NH_2·$[CH_2]_2$·OH and phthalimide at 100°) with PBr_3 at 100° for 2 hr. affords *o*-$C_6H_4(CO)_2N$·$[CH_2]_2$·Br (81%). F. O. H.

Association of ketyls.—See A., 1944, I, 214.

Nuclear acylations according to Friedel–Crafts. II. W. Borsche and J. Barthenheier [with, in part, P. Grotsch] (*Annalen*, 1942, **553**, 250—259).—The possibility is examined that the presence of OAlk may facilitate the acylation of simple C_6H_6 derivatives in which the Friedel–Crafts reaction is inhibited by certain substituents. The following changes are effected usually in gently boiling CS_2: *o*-OMe·C_6H_4·COMe [2 : 4-dinitrophenylhydrazone, m.p. 196—198° (lit. 160°)] to 2 : 4 : 1-$C_6H_3Ac_2$·OH, m.p. 95° (*bis*-2 : 4-*dinitrophenylhydrazone*, decomp. ~320°); *p*-OMe·C_6H_4·COMe (2 : 4-*dinitrophenylhydrazone*, m.p. 233—234°) is unchanged; *o*-OMe·C_6H_4·CO_2Me to unchanged material and *Me* 2-*hydroxy*-5-*acetylbenzoate*, m.p. 6-(2 : 4-*dinitrophenylhydrazone*, m.p. 237—238°); *o*-OMe·C_6H_4·CN to 2-*methoxy*-5-*acetylbenzonitrile*, m.p. 155° (2 : 4-*dinitrophenylhydrazone*, m.p. 283°), with a large amount of initial material containing a small porportion of an unidentified ketone (2 : 4-*dinitrophenylhydrazone*, m.p. 228°); *o*-NO_2·C_6H_4·OMe (in PhNO, instead of CS_2) to 3 : 4 : 1-NO_2·C_6H_3(OMe)·COMe (**I**) (2 : 4-*dinitrophenylhydrazone*, m.p. 262°) and 1 : 3 : 4-CH_2Ph·CO·$C_6H_3(NO_2)$·OMe (**II**) (2 : 4-*dinitrophenylhydrazone*, m.p. 224—225°); *o*-NO_2·C_6H_4·OMe with $[CH_2]_4(COCl)_2$ to α*ζ*-*diketo*-α*ζ*-*di*-3-*nitro*-4-*methoxyphenylhexane*, m.p. 245—246° (*bis*-2 : 4-*dinitrophenylhydrazone*, decomp. 300°); *m*-NO_2·C_6H_4·OMe to *m*-NO_2·C_6H_4·OAc, m.p. 50—51° (lit. 55—56°); *p*-NO_2·C_6H_4·OMe to *p*-NO_2·C_6H_4·OAc, m.p. 79—80°. (**I**) is converted by saturated NH_3–EtOH at 100° into 3-*nitro*-4-*aminoacetophenone*, m.p. 153—154°, reduced (best very rapidly) by H_2 in

presence of Pd–C in MeOH to 3 : 4-*diaminoacetophenone*, m.p. 132—133°, which in warm MeOH is very smoothly transformed by Ac_2 into 6-*acetyl*-2 : 3-*dimethylquinoxaline*, m.p. 117—119°, by Bz_2 into 6-*acetyl*-2 : 3-*diphenylquinoxaline*, m.p. 171—172°, and by phenanthraquinone into 6-*acetyl*-1 : 2-3 : 4-*dibenzophenazine*, m.p. 278°; with boiling AcOH–4N-HCl it gives 5-*acetyl*-2-*methylbenziminazole*, m.p. 190—191° (2 : 4-*dinitrophenylhydrazone*, decomp. 336°), and with 2N-HCl and $NaNO_2$ at 0° it affords 5-*acetylaziminobenzene*, m.p. 164—165° (2 : 4-*dinitrophenylhydrazone*, decomp. 305°). 3-*Nitro*-4-*methylaminoacetophenone*, m.p. 170°, is catalytically reduced to 3-*amino*-4-*methylaminoacetophenone*, m.p. 123—124°, which gives 5-*acetyl*-1-*methylaziminobenzene*, m.p. 144—145°. (**I**) is converted by N_2H_4,H_2O in EtOH at 100° into 3-*nitro*-4-*methoxyacetophenonehydrazone*, m.p. 101°, and 6-*acetylbenzazimidol*, $COMe\cdot C_6H_3<^{N(OH)}_{N}>N$, m.p. 195° (2 : 4-*dinitrophenylhydrazone*, sudden decomp., 242°). SeO_2 and (**II**) in Ac_2O at 160° give 3-*nitro*-4-*methoxybenzil*, m.p. 116—118°, less advantageously obtained by hydrolysis of the resin which results from *p*-$NO\cdot C_6H_4\cdot NMe_2$ and (**II**); 2-*phenyl*-3-3′-*nitro*-4′-*methoxyphenylquinoxaline* has m.p. 155—157°. H. W.

Nuclear acylations according to Friedel–Crafts. III. W. Borsche and F. Sinn (*Annalen*, 1942, **553**, 260—277).—Generally the interposition of two CH_2 groups between the C_6H_6 nucleus and negative substituents such as NO_2, CO, or CN is necessary to overcome the resistance to acylation according to Friedel–Crafts caused by these substituents. The reagents in order of decreasing activity are halogenoacetyl halides, and the halides of aliphatic, aromatic-aliphatic, and aromatic acids. The experiments are performed in CS_2 and with 2 mols. of $AlCl_3$ to 1 mol. of acid chloride or anhydride; the proportion of the latter to the second reactant varies. The mixtures are kept for 14—16 hr. at room temp., gently boiled for a few hr., and worked up as usual. $CH_2Ph\cdot NO_2$ is partly unchanged and partly resinified by acid chlorides. *α-Nitro-β-phenylethane*, b.p. 128—135°/14 mm., from $Ph\cdot[CH_2]_2\cdot I$ and $AgNO_2$ in Et_2O at room temp., and AcCl give a 75% yield of isomeric α-nitro-β-acetylphenylethanes from which the p-*isomeride*, m.p. 29° (2 : 4-*dinitrophenylhydrazone*, m.p. 209—210°), is isolated and identified by oxidation to *p*-$C_6H_4(CO_2H)_2$; with BzCl a small amount of (?) nitrobenzoylphenylethane (2 : 4-*dinitrophenylhydrazone*, m.p. 133—137°) results. $Ph\cdot[CH_2]_3\cdot NO_2$ (**I**) and AcCl yield *α-nitro-γ*-p-*acetylphenylpropane*, m.p. 31—33° (2 : 4-*dinitrophenylhydrazone*, m.p. 196°), oxidised exclusively to *p*-$C_6H_4(CO_2H)_2$ and converted by reduction of its Na salt by $SnCl_2$ and conc. HCl followed by treatment with NH_2OH into the *dioxime*, m.p. 138—139°, of *β-p*-acetylphenylpropaldehyde; the intermediate monoxime could not be hydrolysed satisfactorily to the aldehyde. (**I**) and BzCl readily yield *α-nitro-γ*-p(?)-*benzoylphenylpropane*, b.p. 222—226°/0·6 mm., m.p. 33—35° (2 : 4-*dinitrophenylhydrazone*, m.p. 117°), but reaction occurs less readily with $(CH_2\cdot CO)_2O$, giving *β*-p(?)-*γ′-nitropropylbenzoylpropionic acid*, m.p. 115·5°, converted by N_2H_4,H_2O in MeOH into 3-*keto*-6-p-*γ-nitropropylphenyl*-2 : 3 : 4 : 5-*tetrahydropyridazine*, m.p. 139—140°. Attempted acylation of $Ph\cdot[CH_2]_2\cdot CHO$ leads only to a black resin but its oxime and BzCl give a small yield of *β-p*-benzoylphenylpropionitrile, m.p. 83—84° (2 : 4-*dinitrophenylhydrazone*, m.p. 185°, softens greatly at 164°). CH_2PhBz and AcCl readily give mainly *α-keto-α-phenyl-β*-p-*acetylphenylethane*, m.p. 159—160° [*dioxime*, m.p. 180—182°; *bis*-2 : 4-*dinitrophenylhydrazone*, m.p. 230° after softening; oxidised to a mixture of BzOH and *p*-$C_6H_4(CO_2H)_2$], with a small proportion of m-*acetyldeoxybenzoin*, m.p. 73—74° [*dioxime*, m.p. 135°; oxidised to *m*-$C_6H_4(CO_2H)_2$]. CH_2PhBz and $CH_2Ph\cdot COCl$ yield *phenylacetyldeoxybenzoin*, m.p. 175°, softens at 170°, but CH_2PhBz and BzCl do not react.

[With F. W. Roell.] $Ph\cdot[CH_2]_2\cdot Bz$ and Ac_2O give *α-keto-α-phenyl-γ*-p(?)-*acetylphenylpropane*, m.p. 72—73° (*bis*-2 : 4-*dinitrophenylhydrazone*, m.p. 195°), which with PhCHO and alkali yields *α-keto-α-phenyl-γ*-p(?)-*cinnamoylphenylpropane*, m.p. 98°. *α-Keto-α-phenyl-γ-benzoylphenylpropane*, m.p. 92—93°, is obtained similarly from BzCl. α-Keto-αδ-diphenylbutane, m.p. 57° (from $Ph\cdot[CH_2]_3\cdot CN$ and MgPhBr) (2 : 4-*dinitrophenylhydrazone*, m.p. 145°), and BzCl give *α-keto-α-phenyl-δ-benzoylphenylbutane*, m.p. 79°. $Ph\cdot[CH_2]_4\cdot Bz$ and AcCl give *α-keto-α-phenyl-ε-acetylphenylpentane*, m.p. 65° (*cinnamylidene* derivative, m.p. 90°), whilst BzCl gives *α-keto-α-phenyl-ε-benzoylphenylpentane*, m.p. 58°.

$CH_2Ph\cdot CO_2Et$ is transformed by AcCl followed by esterification into Et *p*-acetylphenylacetate, b.p. 183°/16 mm., m.p. 62—63° (lit. 68—69°). $Ph\cdot[CH_2]_2\cdot CO_2Et$ and AcCl give a mixture of *Et* p(?)-*acetylphenylpropionate*, b.p. 194—197°/16 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 146—147°), and the corresponding *acid*, m.p. 119° [*oxime*, m.p. 151—152°; non-cryst. Me ester (2 : 4-*dinitrophenylhydrazone*, m.p. 163—164°)]; with $CH_2Ph\cdot COCl$ it gives (after esterification) a mixture of isomeric Et phenylacetylphenylpropionates (2 : 4-dinitrophenylhydrazone, m.p. 94—104°) [from which after hydrolysis *β*-p(?)-*phenylacetylphenylpropionic acid*, m.p. 135—136°, is isolated] and (?) *Et phenylacetylphenylacetylpropionate*, $C_{27}H_{26}O_4$, m.p. 143—145°.

[With F. W. Roell.] $Ph\cdot[CH_2]_2\cdot CO_2Me$ and BzCl afford *Me benzoylphenylpropionate*, m.p. 74° (2 : 4-*dinitrophenylhydrazone*, m.p. 136°), hydrolysed to the *acid*, m.p. 97°. $(CH_2\cdot CO)_2O$ converts $CH_2Ph\cdot CO_2Et$ into *β-carbethoxyethylbenzoylpropionic acid*, m.p. 113—114° (corresponding *dicarboxylic acid*, m.p. 193—195°).

$Ph\cdot[CH_2]_2\cdot CN$ with AcCl gives *β*-p-*acetylphenylpropionitrile*, m.p. 44—46° (2 : 4-*dinitrophenylhydrazone*, m.p. 215°), oxidised exclusively to *p*-$C_6H_4(CO_2H)_2$; with $CH_2Ph\cdot COCl$ it yields *β*-p(?)-*phenylacetylphenylpropionitrile*, m.p. 113—115°, accompanied by (?) phenylacetylphenylacetylphenylpropionitrile, b.p. 320—340°/0·6 mm.; with BzCl it affords *β-benzoylphenylpropionitrile*, b.p. ~200°/1 mm., m.p. 83—84°, and with $(CH_2\cdot CO)_2O$ it yields *β*-p-*β′-cyanoethylbenzoylpropionic acid*, m.p. 151—152°, converted by N_2H_4,H_2O in boiling EtOH into 3-*keto*-6-p-*γ-cyanopropylphenyl*-2 : 3 : 4 : 5-*tetrahydropyridazine*, m.p. 173°. H. W.

1 : 2-Addition of magnesium methyl iodide to mesityl ketones. R. C. Fuson, M. D. Armstrong, W. E. Wallace, and J. W. Kneisley (*J. Amer. Chem. Soc.*, 1944, **66**, 681—684).—2 : 4 : 6 : 1-$C_6H_2Me_3\cdot COBu^t$ does not react with MgMeI. 2 : 4 : 6 : 1-$C_6H_2Me_3\cdot COPh$ and MgMeI in boiling Et_2O and then C_6H_6 give, by 1 : 2-addition and spontaneous dehydration, *α-mesitylstyrene* (**I**) (64%), b.p. 120°/3 mm., also obtained in poor yield from COPhMe by 2 : 4 : 6 : 1-$C_6H_2Me_3\cdot MgBr$. H_2–PtO_2 reduces (**I**) in 95% EtOH to *α-phenyl-α-mesitylethane*, b.p. 154—155°/4 mm. With fuming HNO_3 in Ac_2O–AcOH at 0°, (**I**) gives *β-nitro-α*-3-*nitromesitylstyrene* (**II**), m.p. 144—145°, reduced by H_2–PtO_2 in EtOAc to *β-phenyl-β*-3-*nitromesitylvinylamine* (**III**), m.p. 100—101° (*Ac*, m.p. 199—200°, and *Bz* derivative, m.p. 143—144°). $SnCl_2$–conc. HCl–EtOH at the b.p. reduces (**II**) or (**III**) to *di-(β-phenyl-β*-3-*aminomesitylvinyl)amine* (**IV**), m.p. 184—186°. (**III**) is neutral and resists hydrolysis but in HCl–EtOH–H_2O gives *di-(β-phenyl-β*-3-*nitromesitylvinyl)amine*, m.p. 235—236°, also reduced to (**IV**) by $SnCl_2$. *Benzoylisodurene* (prep.: Friedel–Crafts; 78% yield), m.p. 60—61°, b.p. 159—164°/4 mm., with MgMeI as above gives *α*-iso*durylstyrene* (**V**) (42%), b.p. 152—154°/3 mm., and a *substance*, $C_{34}H_{38}O_2$, m.p. 191—192·5°. (**V**) is also obtained (10% yield) from COPhMe by 2 : 3 : 4 : 6 : 1-$C_6HMe_4\cdot MgBr$, with H_2–Raney Ni at 50°/2000 lb. gives *α-phenyl-α*-iso*durylethane*, m.p. 54·5—55°, b.p. 160°/5 mm., and with fuming HNO_3 in Ac_2O–AcOH yields, in 2 days, *ββ-dinitro-α*-5-*nitro*iso*durylstyrene*, m.p. 193—194°. 2 : 4 : 6 : 1-$C_6H_2Me_3\cdot CO\cdot C_6H_4Me$-*p* and MgMeI give impure 2 : 4 : 6 : 1-$C_6H_2Me_3\cdot C(C_6H_4Me\text{-}p):CH_2$ and thence *β-nitro-α*-p-*tolyl-α*-3-*nitromesitylethylene*, m.p. 174—175°. The styrene derivatives are oxidised by $KMnO_4$ or CrO_3 and absorb Br in CCl_4 with slow evolution of HBr. R. S. C.

Normal and *ψ*-esters of *o*-benzoylbenzoic acid types. II. M. S. Newman and B. T. Lord (*J. Amer. Chem. Soc.*, 1944, **66**, 731—732; cf. A., 1942, II, 100).—Normal *forms* of *Me* 2-*benzoyl*- (**I**), m.p. 50·4—51·6°, 2-3′ : 4′-*dimethylbenzoyl*- * (**II**), m.p. 62·6—63·6°, and 2-*mesitoyl*- * (**III**), m.p. 110·8—111·8°, -3 : 6-*dimethylbenzoate* and of o-2′ : 4′-*dimethylbenzoylbenzoate* * (**IV**), m.p. 64·6—65·6°, are obtained from the appropriate acids by CH_2N_2–Et_2O. The *ψ-forms* of (**I**)* m.p. 113·6—114·4°, (**II**) m.p. 86·8—87·2°, and (**IV**), m.p. 62·2—63·2°, are prepared from the acid chlorides by MeOH–C_5H_5N, but (**III**) is formed also by this method. Forms marked * are obtained from the acid by HCl–MeOH. R. S. C.

Behaviour of γ-keto- and aldehydo-acid derivatives at the dropping mercury electrode. I. Esters and anhydrides. S. Wawzonek, H. A. Laitinen, and S. J. Kwiatkowski (*J. Amer. Chem. Soc.*, 1944, **66**, 827—830).—All esters of *o*-$C_6H_4Bz\cdot CO_2H$ (**I**) are reduced polarographically in 0·1M-NBu^n_4I–50% dioxan to α-phenylphthalide, but *n*- and cyclic esters behave differently. Cyclic esters are not hydrolysed in an alkaline buffer ($NMe_4\cdot OH$–NMe_4I–H_3PO_4–50% dioxan) and the half-wave potentials are independent of pH; the ease of reduction increases with increasing ionisation const. of the alcoholic or phenolic component. Me and Et *n*-esters resemble $COPh_2$. Aryl *n*-esters are reduced at ~1·28 v. Anhydrides of (**I**) are also reduced but their behaviour does not permit conclusions as to structure. R. S. C.

Behaviour of 3 : 6-dimethylphthalic anhydride in Friedel–Crafts and Grignard condensations. M. S. Newman and B. T. Lord (*J. Amer. Chem. Soc.*, A., 1944, **66**, 733—735).—2 : 5-Dimethylfuran and $(CH\cdot CO)_2O$ in Et_2O give an adduct, m.p. 59—63°, which with 90% H_2SO_4 at −6° to 0° (later 10°) gives 3 : 6 : 1 : 2-$C_6H_2Me_2(CO)_2O$ (**I**) and some 2 : 5 : 1-$C_6H_3Me_2\cdot CO_2H$. With MgPhBr, 2 : 4 : 1-$C_6H_3Me_2\cdot MgBr$, or 2 : 4 : 6 : 1-$C_6H_2Me_3\cdot MgBr$ in boiling C_6H_6 (1 hr.), (**I**) gives 2-*benzoyl*- (**II**) (81%), m.p. 182·6—183·2°, 2-2′ : 4′-*dimethylbenzoyl*- (**III**) (56%), m.p. 165·2—165·8°, and 2-*mesitoyl*- (**IV**) (44%; 27% in boiling Et_2O in 2 hr.), m.p. 174·8—175·6°, -3 : 6-*dimethylbenzoic acid*, respectively. With $AlCl_3$–C_6H_6, –*m*-xylene, or –mesitylene under optimum conditions (detailed), (**I**) gives (**II**) (57%), (**III**) 96%), or (**IV**) (34%), respectively. The structure of (**IV**) is proved by heating with a little of its Cu salt at 192—195°, yielding 2 : 4 : 6 : 2′ : 5′-*pentamethylbenzophenone*, m.p. 77—78°, which is also obtained from 2 : 5 : 1-$C_6H_3Me_2\cdot COCl$, *s*-$C_6H_3Me_3$, and $AlCl_3$ in CS_2 at room temp. M.p. are corr. R. S. C.

Condensation of chrysene with succinic anhydride. J. W. Cook and W. Graham (*J.C.S.*, 1944, 329—330).—Chrysene, $(CH_2\cdot CO_2)O$, and $AlCl_3$ in $PhNO_2$ at 20° for 6 hr. give *β*-(4- or 5-chrysenoyl)-

propionic acid (I), m.p. 218—221° [and not the 1-derivative as suggested by Beyer (A., 1938, II, 236)], and some β-2-isomeride, m.p. 192—194°. γ-(4- or 5-Chrysenyl)butyric acid, m.p. 210·5—212·5° (cf. *loc. cit.*), is converted by PCl_5–C_6H_6, then $SnCl_4$, at room temp. for 20 hr. into 5′- or 8′-*keto*-5′ : 6′ : 7′ : 8′-*tetrahydro*-1 : 2-(2′ : 3′-*naphtha*)*phenanthrene*, decomp. >275°. This with N_2H_4,H_2O in NaOEt–EtOH at 200° in a sealed tube gives 5′ : 6′ : 7′ : 8′-*tetrahydro*-1 : 2-(2′ : 3′-*naphtha*)*phenanthrene*, m.p. 217—218°, dehydrogenated by Pd–C at 300° (sealed tube; vac.) to 1 : 2-(2′ : 3′-naphtha)phenanthrene, m.p. 292—294° (2 : 7-dinitroanthraquinone *complex*, m.p. 278—279°). A. T. P.

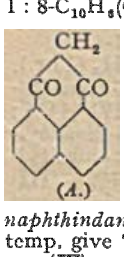
Equilibrium mixture of *cis*- and *trans*-2 : 6-dimethyl*cyclo*hexanone. R. Cornubert and P. Anziani (*Compt. rend.*, 1943, **217**, 197—199).—The methods (lit.) of prep. of 2 : 6-dimethyl*cyclo*hexanone (I) give an equilibrium mixture of *cis*- and *trans*-isomerides. Ring-contraction probably occurs in the supposed prep. of (I) by the method of Ruzicka *et al.* (A., 1931, 1302) from 1 : 3-dimethyl-Δ³-*cyclo*hexene. F. R. S.

Orientation phenomena during reduction of a cyclanone or its oxime. P. Anziani and R. Cornubert (*Compt. rend.*, 1943, **217**, 233—235).—Reduction of 2 : 6-dimethyl*cyclo*hexanone (I), using Pt in acid, alkaline, or neutral solution, gives the same alcohol (phenylurethane, m.p. 158°), whilst Na in moist Et_2O, EtOH, or BuOH leads to a phenylurethane, m.p. 132° (cf. Skita, A., 1924, i, 25). Reduction of the oxime, m.p. 79°, of (I) with H_2–Pt-black in AcOH–HCl or in a neutral medium gives an amine differing from that formed with Na–EtOH. It is concluded that the isomeride obtained does not depend on the acid medium but rather on the use of Pt. F. R. S.

[**Ionones.**] (A) L. Palfray, (B) Y. R. Naves and P. Bachmann (*Helv. Chim. Acta*, 1944, **27**, 626).—(A) A reply to the criticisms by Naves and Bachmann (A., 1944, II, 103) of the paper by Kandel (A., 1939, II, 169).
(B) A reply. J. W. S.

Reaction between cyclic β-diketones and Grignard reagents. III. 2-Benzoyl-2-methyl-1-hydrindone. T. A. Geissman and V. Tulagin (*J. Amer. Chem. Soc.*, 1944, **66**, 719—722).—Keeping $CH_2Ph{\cdot}CH(CO_2Et)_2$, MeI, and NaOEt in C_6H_6 and then hydrolysing by hot NaOH–EtOH–H_2O gives $CH_2Ph{\cdot}CMe(CO_2H)_2$ (80%), m.p. 139·5—140° (lit. 135°), which with, successively, $SOCl_2$–C_5H_5N (little)–C_6H_6, PCl_5–C_6H_6, and $AlCl_3$–C_6H_6 yields 2-*benzoyl*-2-*methyl*-1-*hydrindone* (1) (good yield), m.p. 62·5—63·5°. The structure of (I) is proved by cleavage by boiling 30% NaOH to BzOH and 2-methyl-1-hydrindone (II). Interaction of (I) with MgPhBr in boiling C_6H_6–Et_2O gives 1-*hydroxy*-1-*phenyl*-2-α-*hydroxybenzhydryl*-2-*methylhydrindane* (III) (4 pts.), m.p. 214—215°, and $CPh_3{\cdot}OH$ + (II) (1 pt. each). Thus, formation of a chelated intermediate does not alone suffice to produce cleavage of β-diktones by MgRHal. The structure of (III) is proved by oxidation by boiling aq. HNO_3 to $COPh_2$ and *o*-$C_6H_4Bz{\cdot}CO_2H$ as sole products. $CHPh_2{\cdot}CNa(CO_2Et)_2$ and MeI in Et_2O give an ester, hydrolysed to *benzhydrylmethylmalonic acid*, m.p. 143—145° (gas), which with PCl_5–C_6H_6 and then $AlCl_3$ or $SnCl_4$ in C_6H_6 gives 1 : 3-*diphenyl*-2-*methylhydrindene*, m.p. 91—92°, but in CS_2 gives a tar. $(CH_2Ph)_2CH{\cdot}CO_2H$ with $SOCl_2$–C_6H_6–C_5H_5N and then CH_2N_2 gives a *diazo-ketone*, m.p. 72—74°, and thence γγ′-*diphenylisovaleric acid*, m.p. 85—86° (obtained also less well by a Reformatsky reaction), which by ring-closure ($SOCl_2$; $SnCl_4$–C_6H_6) yields 1-*keto*-3-*benzyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 54—56°. This gives the *Me* 2-*glyoxylate*, m.p. 85—87°, converted by heating with soft glass at 175° into *Me* 1-*keto*-3-*benzyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-2-*carboxylate*, m.p. 77—78°. MeI–NaOMe–C_6H_6 then gives *Me* 1-*keto*-3-*benzyl*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-2-*carboxylate*, m.p. 114—115°, hydrolysis of which is difficult. R. S. C.

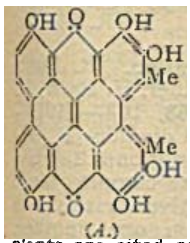
Reaction between cyclic β-diketones and Grignard reagents. II. 8 : 8-Dimethylperinaphthindane-7 : 9-dione. T. A. Geissman and L. Morris (*J. Amer. Chem. Soc.*, 1944, **66**, 716—719; cf. A., 1942, II, 146).—1 : 8-$C_{10}H_6(CO)_2O$ with KOH–Me_2SO_4–MeOH gives 89% of 1 : 8-$C_{10}H_6(CO_2Me)_2$ (I) and with $CH_2(CO_2Et)_2$–$ZnCl_2$ at 170—175° gives perinaphthindane-7 : 9-dione (*A*), new m.p. 247° (decomp.), which with MeI–NaOEt–EtOH at 100° gives 8-*methyl*- (60%), m.p. 183—185° [obtained in very poor yield from (I) by $EtCO_2Et$–Na], and thence by MeI–NaOMe–$COMe_2$–MeOH (little) at the b.p. gives 8 : 8-dimethyl-perinaphthindane-7 : 9-dione (II) (30—40%), m.p. 99—101° (2 : 4-*dinitrophenylhydrazone*, m.p. 208—210°). Adding MgPhBr (1 mol.) to (II) in Et_2O–C_6H_6 at 0° gives slowly 7-*hydroxy*-7-*phenyl*-8 : 8-*dimethylperinaphthindan*-9-*one* (III), m.p. 190°, but 3 mols. of MgPhBr at room temp. give 7 : 9-*dihydroxy*-7 : 9-*diphenyl*-8 : 8-*dimethylperinaphthindane* (IV), m.p. 168°, or at 80° give 7-*hydroxy*-1 : 7-*diphenyl*-8 : 8-*dimethylperinaphthindan*-9-*one* (V), m.p. 238—239°. With a drop of conc. HCl in boiling MeOH, (III) or (V) gives its *Me ether*, m.p. 214—216° or 224°, respectively, and with HCl–$CaCl_2$–C_6H_6 gives the 7-*Cl*-derivative, m.p. 156° (decomp.) or 158—162° (decomp.), respectively. A trace of HCl in MeOH at the b.p. converts (IV) into the 7 : 9-*epoxy*-compound, m.p. 134°. Structures are confirmed by behaviour in the Grignard machine. R. S. C.



(A.)

Hypericin, the photodynamic pigment of St. John's wort (*Hypericum perforatum*). H. Brockmann, F. Pohl, K. Maier, and M. N. Haschad (*Annalen*, 1942, **553**, 1—52; cf., A., 1939, 483).—*Hypericin* (I) appears to be a hexahydroxy-2 : 2′-dimethylnaphthadianthrone. Extraction of the dried blossoms of *H. perforatum* with Et_2O removes chlorophyll and carotenoids, after which (I) is removed from the residue by MeOH. From this solution it is obtained cryst. by addition of HCl–MeOH and is subsequently cryst. by adding HCl–MeOH to the solution in C_5H_5N. The blue-black pigment has no definite m.p. but decomposes at >330° and cannot be sublimed in a high vac. The marked red fluorescence of its solutions in C_5H_5N disappears on addition of acid. (I) gives green solutions in alkali, sensitive to air. Adsorption on CaC_2O_4 shows that (I) is homogeneous. (I) does not contain OMe. Oxidation (Kuhn–Roth) affords AcOH. Analyses and determinations of the mol. wt. of the *hexabenzoate* (II), m.p. ~228°, and *hexa*-p-*bromobenzoate*, m.p. ~270° [from (I) and the requisite chloride in C_5H_5N], establish the formula $C_{30}H_{16}O_8$ or, possibly, $C_{30}H_{18}O_8$. (I) is scarcely attacked by CH_2N_2 and is so sensitive to alkali that it cannot be methylated by Me_2SO_4 or MeI. With Ac_2O in C_5H_5N (I) affords a difficultly cryst., unstable acetate. (II) is insol. in cold Claisen solution. The remaining two O atoms are present in the quinone group since reductive benzoylation leads to an amorphous *octabenzoate*. Oxidation of (I) readily leads to small fragments. Distillation of (I) with Zn dust gives very small amounts of a red sublimate (III), also formed in very small yield when (I) is heated with conc. HI at 200° and the product dehydrogenated by Cu powder at 400° or Pd–asbestos at 350°, or when (I) is heated with Zn dust in molten $ZnCl_2$–NaCl. The amount of (III) obtained is too small for analysis but it is identified by absorption spectrum, fluorescence, chromatography and mixed chromatography (over Al_2O_3 II), and behaviour towards Br as *meso*anthrodianthrene. This cannot, however, be the parent hydrocarbon of (I) since it is not in accord with the % of H or the presence of 2 Me. During the formation of (III) a new ring must be formed by participation of the 2 Me so that the parent material is either 2 : 2′-dimethyl*meso*benzdianthrene or 2 : 2′-dimethylnaphthadianthrene and (I) is consequently a $(OH)_6$-derivative of 2 : 2′-dimethylhelianthrone (IV) or of 2 : 2′-dimethyl*meso*naphthadianthrone (V). Model experiments show that (III) is produced in somewhat better yield than from (I) when (IV) or (V) is reduced with HI and then dehydrogenated. Distillation of (IV) or (V) with Zn dust also gives (III) whereas treatment of (IV) with Zn dust in molten NaCl–$ZnCl_2$ or distillation of (IV) with Zn dust in a high vac. gives 2 : 2′-*dimethylbenzdianthrene* (VI) in addition to (III); under the same conditions (IV) gives (III) with a small proportion of blue 2 : 2′-*dimethyl*meso*naphthadianthrene* (VII). Under all experimental conditions naphthadianthrone yields exclusively the blue naphthadianthrene whereas, in addition, meso*benzdianthrene* is obtained when helianthrone is distilled with Zn dust in a high vac. or treated with Zn dust in molten $ZnCl_2$–NaCl. It does not appear possible under any conditions to obtain (VI) or (VII) from (I); this observation supports the naphthadianthrone structure for (I). Attempts to discriminate between the helianthrone and naphthadianthrone structures for (I) based on oxidation, behaviour towards conc. H_2SO_4, and photochemical behaviour of (I) and its derivatives and helianthrone and its compounds do not give well defined results. The acetates of reduced helianthrone and its 2 : 2′-Me_2 derivative and of (V) have nearly the same absorption bands and therefore nearly the same colour as the corresponding parent hydrocarbons, one of which is red and the other blue. Reductive acetylation therefore affords a ready means of discriminating between a helianthrone and naphthadianthrone. Acetylating reduction of (II) gives a blue Ac derivative with bands very similar to those of (VII) or its 10 : 10′-$(OAc)_2$-derivative. If, therefore, the OBz groups do not influence appreciably the position of the absorption bands it follows with certainty that (I) is a hexahydroxy-2 : 2′-dimethylnaphthadianthrone. The behaviour of the dibenzoate of 4 : 4′-dihydroxyhelianthrone when reductively acetylated appears to show that this is the case but the dibenzoate of 4 : 4′-dihydroxynaphthadianthrone could not be investigated on account of the sparing solubility. Further experiments are required to enable a definite decision to be made. Distillation of (I) with Zn dust can proceed beyond the formation of (III), giving yellow or colourless H_4- or H_6-derivatives which are invariably obtained as final products of reductive acetylation in C_5H_5N; in Ac_2O these are obtained only from hydroxylated quinones and only when C_5H_5N is present, whereas OH-free quinones are not reduced beyond the coloured stage. (I) is not sensibly reduced by Zn dust in AcOH at room temp. and resembles in this respect many polynuclear quinones which do not give vats; in C_5H_5N containing a little AcOH in absence of air (I) gives a brown-red solution with ill-defined absorption bands. Addition of B_2O_3–Ac_2O to the red solution of (I) in Ac_2O causes immediate formation of a green solution with red fluorescence and new, well-marked absorption bands, thus indicating the presence of at least two α-OH groups. Warming the green solution causes slight displacement of the bands

towards shorter λ but the green colour persists. One or more 6-OH are therefore considered to have been acetylated but the acetylation remains incomplete since identical products are not obtained thus and by the action of B_2O_3–Ac_2O on the acetate or benzoate of (**I**). The colours of the solutions suggest that the green solution contains one or two α-OH groups in addition to those esterified by B_2O_3–Ac_2O. (The possibility of the replacement of Ac or Bz groups during the action of B_2O_3–Ac_2O is established by experiments with quinizarin, chrysazin, and anthrarufin.) The annexed structure (*A*) is therefore tentatively suggested for (**I**). Other examples of the presence of polynuclear compounds in plants are cited and suggestions for their genesis under biological conditions are discussed. (See also A., 1944, III, 708.) H. W.



(*A*)

IV.—STEROLS AND STEROID SAPOGENINS.

Preparation of steroidal carbinols.—See B., 1944, III, 169.

Neutral, non-saponifiable fraction of ox-bile. W. H. Pearlman (*J. Amer. Chem. Soc.*, 1944, **66**, 806—809).—Inspissated ox-bile (15 kg.; 70% solids) yields a non-saponifiable fraction, whence are obtained cholesterol (>50 g.) and *alcohols A*, $C_{27}H_{40}O_3$ (40 mg.), m.p. 300° {*acetate*, m.p. 216—217°; benzoate, m.p. 155—157° [absorption max. at 2310 (ε 13,470) and 2720 A. (ε 973)]}, *B* [? a 3(β)-hydroxy*allo*pregnane derivative], $C_{21}H_{36}O_2$ (15 mg.), m.p. 192—193° {digitonide; *dibenzoate*, m.p. 234—235° [absorption max. at 2310 (ε 27,700) and 2720 A. (ε 1985)]}, *C*, $C_{25-26}H_{40-42}O_4$ (46 mg.), m.p. 255—257° [*acetate*, m.p. 187°, with KOH in 90% MeOH regenerates *C* (m.p. 260°)], *D*, $C_{24}H_{40}O_3$ (28 mg.), m.p. 232—233° (*acetate*, m.p. 111°, $[\alpha]_D^{18}$ +72° in EtOH), and *E*, $C_{24}H_{42}O_4$ (20 mg.), m.p. 202° (an impure fraction, m.p. 204—206°, had $[\alpha]_D$ +37° in EtOH) (*diacetate*, m.p. 142·5°). Pregnane-3(β) : 20(α)-diol has m.p. 182° (cf. Marker *et al.*, A., 1938, II, 12) and gives a *dibenzoate*, m.p. 167—168°. M.p. are corr. R. S. C.

Sterols of *Calycanthus floridus*. J. W. Cook and M. F. C. Paige (*J.C.S.*, 1944, 336—337).—Unsaponifiable components comprise ~1·6% of the oil extracted by C_6H_6 from the seeds of *C. floridus*. Hydrolysis is carried out by boiling KOH–MeOH for 8 hr. The phytosterol mixture, mainly m.p. 135—137°, consists of <70% of β-sitosterol, m.p. 137·5—138·5°, $[\alpha]_D^{18}$ −34° in $CHCl_3$ (isolated through the benzoate), a little α-sitosterol, and probably sitostanol, but no stigmasterol. Incomplete reduction (Meerwein–Ponndorff) of 7-ketocholesteryl acetate and benzoylation gives 7-hydroxycholesterol dibenzoate (**I**) and some 7-*ketocholesteryl benzoate*, m.p. 159·5—161°, the opaque liquid then becoming green at 182·5° and colourless and clear at 183·5°, also obtained from 7-ketocholesterol and BzCl–C_5H_5N at room temp. (**I**) and boiling NPhMe$_2$ (8 hr.) yield 7-dehydrocholesteryl benzoate, which is converted into α- and thence into β-cholestenyl benzoate (cf. Schenck *et al.*, A., 1937, II, 59), which is hydrogenated (PtO_2–AcOH–Et_2O) to *cholestanyl hexahydrobenzoate*, m.p. 158·5—159°, hydrolysed to hexahydrobenzoic acid, m.p. 29—30°, and cholestanol, m.p. 141·5—142·5°. The *trans*-configuration assigned to the C–D ring fusion of the sterols is probably correct. A. T. P.

Sterol, m.p. 155—157°, $[\alpha]_D^{25}$ −55·8° in $CHCl_3$ (acetate, m.p. 134—135° : 3 : 5-dinitrobenzoate, m.p. 222—223°, $[\alpha]_D$ −17·3° in $CHCl_3$), from the common bean, *Phaseolus vulgaris*.—See A., 1944, III, 624.

Lactones of the *cyclo*pentanopolyhydrophenanthrene series.—See B., 1944, III, 168.

Preparation of 24-keto- and 24-hydroxy-cholesterol and [their] derivatives. B. Riegel and I. A. Kaye (*J. Amer. Chem. Soc.*, 1944, **66**, 723—724).—3-Acetoxy-Δ^5-cholenyl chloride with CdPr$^\beta_2$–Et_2O and then KOH–MeOH gives 24-*ketocholesterol* (**I**) (53%), m.p. 137—138·5°, $[\alpha]_D^{26}$ −37° in $CHCl_3$ {*acetate* (**II**), m.p. 127·5—128° (not fluid), turbid 129—130°, meniscus formed at 131°, $[\alpha]_D^{26}$ −41° in $CHCl_3$ (*oxime*, softens 155°, m.p. 156—158·5°); *semicarbazone*, m.p. 166—168°}, which is a good starting point for sterol syntheses. With 85% N_2H_4,H_2O and NaOEt in EtOH at 200°, (**I**) gives cholesterol. Al(OPr$^\beta$)$_3$–Pr$^\beta$OH at the b.p. reduces (**II**), with hydrolysis, to 24-*hydroxycholesterol* (94%), m.p. 166—169°, which yields only the *diacetate*, softens 93°, m.p. 95—96°. The 3-p-*toluenesulphonate*, softens 115°, m.p. 119—120° (decomp.), $[\alpha]_D^{26}$ −35° in $CHCl_3$, of (**I**) with dry KOAc in boiling MeOH gives 24-*keto*-i-*cholesteryl Me ether* (53%), m.p. 90·5—91·5°, $[\alpha]_D^6$ +52° in $CHCl_3$, reduced by Al(OPr$^\beta$)$_3$–Pr$^\beta$OH to 24-*hydroxy*-i-*cholesteryl Me ether*, an oil, $[\alpha]_D^{27·5}$ +31° in $CHCl_3$. M.p. are corr. R. S. C.

V.—TERPENES AND TRITERPENOID SAPOGENINS.

Rearrangements in the terpene series. I. Isomerisation and esterification of α-pinene. M. S. Kharasch and W. B. Reynolds (*J. Chem.*, 1944, **9**, 148—154).—α-Pinene (**I**) is heated at 135—140° with *p*-OMe·C_6H_4·CO_2H, CHPh:CH·CO_2H, BzOH, *o*-OMe·C_6H_4·CO_2H, 1-$C_{10}H_7$·CO_2H, OEt·CH_2·CO_2H, *o*- and *m*-NO_2·C_6H_4·CO_2H, *o*-C_6H_4Bz·CO_2H, *o*-OH·C_6H_4·CO_2H, *o*-C_6H_4Cl·CO_2H, *o*-C_6H_4Br·CO_2H, 3 : 5 : 1-$(NO_2)_2C_6H_3$·CO_2H, CH_2Cl·CO_2H, 2 : 5 : 1-OH·C_6H_3Br·CO_2H, 2 : 4 : 1-$(NO_2)_2C_6H_3$·CO_2H, or CCl_3·CO_2H. The terpene, largely *d*-limonene, is removed with steam, the residual ester is hydrolysed, and the liberated borneol with a small proportion of *iso*borneol is determined. High yields under these conditions are obtained over a very narrow range of ionisation const., $K = 3·7 \times 10^4$ to 8×10^4. At higher temp. acids with lower K are fairly effective. The yields of bornyl esters formed by acids of < optimum K (*e.g.*, BzOH) are greatly improved by addition of *o*-$C_6H_4(OH)_2$, *o*- and *m*-cresol, PhOH, β-$C_{10}H_7$·OH, resorcinol, and *p*-NO_2·C_6H_4·OH, but not of PhOMe, $PhNO_2$, quinoline, or PhCN at 140°. This improvement is due to increased availability of H^+, not to increase in the dielectric const. of the reaction medium or to isomerisation of (**I**) to camphene. *d*-α-Pinene when heated with a mixture of an org. acid and amide is converted into *d*-limonene in good yield; the amide appears to inhibit esterification. The principal products formed in the reaction of (**I**) with org. acids can be explained by assuming the preliminary capture of a proton by (**I**); the unstable ion thus formed rearranges and stabilises itself in various ways. H. W.

Synthetic production of camphor from pinene. B. G. S. Acharya (*J. Univ. Bombay*, 1944, **12**, A, Part 5, 29—30; cf. A., 1943, II, 239).—Pinene hydrochloride (1 mol.), dry Na stearate (2 mols.), Na_2CO_3 (1 mol.), and NaOH (1 mol.), refluxed for 24 hr. and distilled, give camphene (**I**) in 90% yield, convertible into camphor without further purification. A slight increase in yield is obtained by working in N_2 and distilling under reduced pressure. Residues from distillation can be used again for 8—9 times. Yields of (**I**) using mowda, coconut, ground-nut, castor, linseed, and cottonseed oil, and mutton tallow in place of stearic acid are 90, 84, 69, 73, 71, 68, and 87%, respectively. A. T. P.

VI.—HETEROCYCLIC.

Furfurylamines.—See B., 1944, II, 198.

Terpene ethers etc.—See B., 1944, II, 198.

Acetylene derivatives. XXII. Condensation of dimethylvinylethinylcarbinol and vinyl*iso*propenylacetylene with *o*- and *p*-cresol. I. N. Nazarov and F. I. Gotman. **XXIII. Dimerisation of dimethylvinylethinylcarbinol to 1 : 1 : 3 : 3-tetramethyl-4-vinyl*iso*coumarone with elimination of water.** I. N. Nazarov and G. P. Vercholetova (*Bull. Acad. Sci. U.R.S.S., Cl. Sci. Chim.*, 1941, 545—555, 556—572).—XXII. *o*-Cresol condenses with dimethylvinylethinylcarbinol (**I**) or vinyl*iso*propenylacetylene (**II**) (H_3PO_4 catalyst) in the same way as phenol (*ibid.*, 1940, 314) giving the readily polymerised p-[α*α*-*dimethyl*-α-(*vinylethinyl*)]-*o*-*cresol*, b.p. 129—130°/2 mm. The *Me ether*, b.p. 115—116°/2 mm., m.p. 30—30·5°, is oxidised by $KMnO_4$ in $COMe_2$ to $H_2C_2O_4$ and α-(4-*methoxy*-3-*methylphenyl*)iso*butyric acid*, m.p. 108°, further oxidised by HNO_3 to 4-methoxy-3-methylbenzoic acid.

m-Cresol condenses with (**I**) or (**II**) giving about equal amounts of neutral and acidic products. The latter contain p-[α*α*-*dimethyl*-α-(*vinylethinyl*)]-m-*cresol* (**III**) (*phenylurethane*, m.p. 112—112·5°), which is readily polymerised and is hydrogenated to 3-*methyl*-4-α*α*-*dimethylamylphenol*, b.p. 138—140°/3 mm. The *Me ether* of (**III**), also obtainable from *m*-C_6H_4Me·OMe and (**I**) or (**II**), b.p. 125—126°/3 mm., is oxidised to $H_2C_2O_4$ and (impure) α-(4-*methoxy*-2-*methylphenyl*)iso*butyric acid*, further oxidised to 4-methoxy-2-methylbenzoic acid. The neutral product of the reaction is 3 : 3 : 6-*trimethyl*-2-*allylidenecoumarone* (**IV**), b.p. 122·5—123°/7 mm. (**IV**) is hydrogenated to 3 : 3 : 6-*trimethyl*-2-*propylcoumarone*, b.p. 114—114·5°/6·5 mm., and ozonised to 2-*keto*-2 : 3 : 6-*trimethylcoumarone* (**V**), b.p. 114°/8 mm., sometimes accompanied by an *aldehyde*, $C_{13}H_{14}O_2$. (**V**) is hydrolysed by alkali to α-(2-*hydroxy*-4-*methylphenyl*)iso*butyric acid*, m.p. ~145° with reconversion into (**V**), and by NH_3 to the *amide*, m.p. ~150°. Opening of the lactone ring of (**V**) followed by methylation affords α-(2-*methoxy*-4-*methylphenyl*)-iso*butyric acid*, m.p. 136—136·5°, oxidised by HNO_3 to a *nitromethoxytoluic acid*, m.p. 220—220·5°.

XXIII. The compound previously obtained in small amount from (**I**) with H_2SO_4 or Ac_2O can be obtained in 70—80% yield by the action of HCO_2H, H_3PO_4, or $FeCl_3$ in C_6H_6; it is 1 : 1 : 3 : 3-*tetramethyl*-4-*vinyl*iso*coumarone* (**VI**), b.p. 81°/3·5 mm., polymerised to a glass. It forms a *hydrochloride*, m.p. 88·25°, and a *dibromide*, m.p. 109·5°, and is oxidised by $KMnO_4$ to 1 : 1 : 3 : 3-*tetramethyliso*-*coumarone*-4-*carboxylic acid*, m.p. 190—191°, whilst ozonisation also affords the corresponding *aldehyde*, b.p. 105—106°/6·5 mm., m.p. 52—53°, and HCO_2H. (**VI**) is hydrogenated to 1 : 1 : 3 : 3-*tetramethyl*-4-*ethyl*iso*coumarone* (**VII**), b.p. 78—79°/3·5 mm., which on further reduction (Ni catalyst, 6 hr. at 130—140° and 2 hr. at 160°) gives a *product*, $C_{14}H_{22}O$, probably (ethyl*iso*propylphenyl)dimethyl carbinol, m.p. 25—25·5°. At higher temp. hydrogenation of the nucleus also takes place and one of the products, b.p. 182—186°, appears to be ethyl*iso*propyl*cyclo*hexane. G. A. R. K.

Formation of a chromone by the von Pechmann condensation of ethyl acetoacetate with 2-chloro-*m*-5-xylenol. R. Adams and J. W. Mecorney (*J. Amer. Chem. Soc.*, 1944, **66**, 802—805).—1 : 3 : 2 : 5-

$C_6H_2Me_2Cl{\cdot}OH$ (**I**) and $CH_2Ac{\cdot}CO_2Et$ in conc. H_2SO_4 at 100° (30 min.) and then room temp. (1 week) give 6-*chloro*-2 : 5 : 7-*trimethylchromone* (**II**) (35%), m.p. 145—146° (and an oil), the structure of which is proved as follows. (**II**) gives a 2-*styryl*-compound, m.p. 186—186·5°, with hot KOH–EtOH gives 2-*chloro*-4-*acetoacetyl*-m-5-*xylenol* (**III**) (45%), m.p. 148—150° [transient red $FeCl_3$ colour in AcOH (not H_2O, EtOH, or $COMe_2$); in warm AcOH + a drop of conc. HCl regenerates (**II**)], and with boiling aq. NaOH gives 5 : 1 : 3 : 2 : 4-$OH{\cdot}C_6HMe_2Cl{\cdot}COMe$ (**IV**), dimorphic, m.p. 106—110° and 89·5—90° (clear at 110°) (cf. lit.) (known Me ether, m.p. 76—77°). Ac_2O–H_2SO_4 at 100° converts (**I**) into its acetate, m.p. 48°, whence $AlCl_3$ at 50° yields (**IV**), which with Na and EtOAc gives (**III**). 4 : 5 : 7-Trimethylcoumarin, m.p. 181° (lit. 175—176°), and H_2SO_4–HNO_3 at −5° to −10° give the 6-NO_2- (80%), m.p. 209—211° (lit. 208°), and thence (Sn–$SnCl_2$–conc. HCl–EtOH at room temp. or, less well, Fe powder in 75% EtOH) the 6-NH_2- (64%), m.p. 199—200°, and (diazo-reaction) 6-*Cl*-derivative (83%), m.p. 194—195·5°, whence O_3 in EtOAc–MeOH and then NaOH–aq. MeOH yields (**IV**). M.p. are corr. R. S. C.

Brominated 4-hydroxycoumarins. C. F. Huebner and K. P. Link (*J. Amer. Chem. Soc.*, 1944, **66**, 656).—Heating $CH_2Ph{\cdot}COCl$ and 2 : 5 : 1-$OH{\cdot}C_6H_3Br{\cdot}CO_2Me$ at the b.p. and then further with C_5H_5N gives *Me* 5-*bromo*-2-*phenylacetoxybenzoate*, m.p. 68—70°, which with Na at 200° yields 6-*bromo*-4-*hydroxy*-3-*phenylcoumarin*, m.p. 252—254°, which crystallises from H_2O at pH 5—6. *Me* 5-*bromo*-2-*acetoxybenzoate*, m.p. 33—35°, with Na in kerosene at 200° gives 6-bromo-4-hydroxycoumarin, which with an excess of CH_2O in boiling EtOH yields 3 : 3′-*methylenebis*-6-*bromo*-4-*hydroxycoumarin*, m.p. 326—327° (*Me*$_2$ *ether*, m.p. 218—220°). R. S. C.

Chemistry and biochemistry of plant materials. IX. Formation of dihydroflavonol and flavonol and synthesis of chalkone–flavanone–flavonol glucosides. L. Reichel and J. Stevdel (*Annalen*, 1942, **553**, 83—97).—The inter-relationships of *o*-hydroxychalkone (**I**), flavanone (**II**), flavonol (**III**), and dihydroflavonol (**IV**) have been examined. Under the experimental conditions (**I**) is quantitatively converted by ½ mol. of NaOH into (**II**) whereas with 1 mol. of NaOH (**I**) is unchanged, and (**II**) is converted completely into (**I**). Direct oxidation of (**II**) to (**III**) by H_2O_2 does not therefore occur; H_2O_2 reacts exclusively with (**I**). (**IV**) is formed from (**I**) suspended in MeOH by the action of alkaline H_2O_2 at room temp. With ⅛ mol. of NaOH and 5 mols. of H_2O_2 the yield of (**IV**) is small; it is good (~50%) with ¼ mol. of NaOH; with 1 mol. of NaOH the yield is 8%, with 11% of (**III**). (**IV**) is dehydrogenated by alkaline H_2O_2 or by mol. O_2 to (**III**). A new autoxidisable system is represented by (**IV**); H_2O_2 produced by dehydrogenation autoxidation is identified by catalase. (**IV**) is an intermediate in the synthesis of (**III**). (**II**) and ¼ mol. of NaOH give traces of (**III**) with 93% of unchanged (**II**). With 2 mols. of NaOH the products are 75% of (**II**) and 19% of (**III**); (**IV**) could never be identified and appears to be dehydrogenated to (**III**) under the experimental conditions. Under corresponding conditions (**II**) and 2 mols. of NaOH afford 46·2% of (**I**), which is an intermediate in the synthesis of (**III**). In 0·01M. solution in MeOH, (**I**), ½ mol. of NaOH, and 1 mol. of H_2O_2 give 67·9% of (**II**) in 18 days at room temp. Production of (**IV**) is first observed with 10 mols. of H_2O_2, the yield being 13·4% with 69·6% of (**II**). With increasing [OH'] isomerisation of (**I**) to (**II**) proceeds more slowly until finally (**I**) remains unchanged. With ¼ mol. of NaOH and 1 mol. of H_2O_2 (**III**) is formed in 29% yield. With 1 mol. of NaOH the yield is only slightly increased. (**IV**) cannot be detected since it is dehydrogenated to (**III**). (**II**) is unchanged by ½ mol. of NaOH and 10 mols. of H_2O_2; under these conditions it is not transformed into (**I**). 20% of (**III**) is formed by use of 1 mol. of NaOH and 2 mols. of H_2O_2. An electronic explanation of the changes is advanced. H. W.

Dibenzfuran. XX. 2 : 3 : 6 : 7-Derivatives. H. Gilman, J. Swiss, H. B. Willis, and F. A. Yeoman (*J. Amer. Chem. Soc.*, 1944, **66**, 798—801; cf. A., 1939, II, 342).—3 : 6-Dibromodibenzfuran, NaOH, Cu-bronze, Cu, and $CuSO_4{,}5H_2O$ at 235—240° give impure 3 : 5-dihydroxy- and thence (Me_2SO_4–NaOH) 3 : 6-*dimethoxy*-*dibenzfuran* (45·5% over-all), m.p. 88—89°. With Br–AcOH at room temp. this gives 4 : 5- (? 4 : 7-) (2 pts.), m.p. 196—197°, and 2 : 7-*dibromo*-3 : 6-*dimethoxydibenzfuran* (**I**) (1 pt.), m.p. 260—261°. With $LiBu^a$ and then Me_2SO_4 in Et_2O–C_6H_6, (**I**) gives 3 : 6-dimethoxy-, m.p. 144—145°, and thence by HBr–AcOH–H_2O 3 : 6-dihydroxy-2 : 7-dimethyldibenzfuran (**II**), sinters 228°, m.p. 231—232°. 1 : 4 : 2 : 5-$C_6H_2MeI(OMe)_2$ (**III**) and Cu give [2 : 5 : 4 : 1-$(OMe)_2C_6H_2Me{\cdot}]_2$ (50—84%), m.p. 134° (cf. Erdtmann, A., 1936, 184), whence HBr–AcOH gives a very small yield of (**II**). CuCN and (**III**) at 240° give 2 : 5-*dimethoxy*-p-*tolunitrile* (73%), m.p. 130—131°, hydrolysed by NaOH–EtOH–H_2O to the *acid* (41%), m.p. 125—126°, which is also obtained (35% yield) from (**III**) by $LiBu^a$ (not by the Grignard reagent) and then CO_2 and is oxidised by aq. $KMnO_4$ to 2 : 5 : 1 : 4-$(OMe)_2C_6H_2(CO_2H)_2$, thus proving the orientation of (**I**)—(**III**). 1 : 2 : 5-$C_6H_3Me(OMe)_2$ gives 4 : 1 : 2 : 5-$NO_2{\cdot}C_6H_2Me(OMe)_2$ (**IV**), hydrogenated (Raney Ni; EtOH; 100°/30—45 lb.) to the unstable amine, m.p. 108·5—109·5° (*Ac* derivative, m.p. 160—162°), whence (**III**) is obtained by a diazo-reaction, thus proving the orientation of (**IV**). Br and a trace of Fe in CCl_4 convert (**IV**) into 1 : 4 : 2 : 5-$C_6H_2MeBr(OMe)_2$, m.p. 168°, whence HBr–AcOH and then Ac_2O give 1 : 4 : 2 : 5-$C_6H_2MeBr(OAc)_2$, m.p. 253—254°. Conc. HNO_3 in AcOH at 45° converts 2 : 5 : 1 : 4-$(OMe)_2C_6H_2Me{\cdot}CO_2H$ or (**III**) into (**V**). R. S. C.

Dinaphthylene dioxide. III. Acylation and nitration. R. Pummerer, E. Buchta, W. Gündel, W. Kiessling, K. Pfeiffer, H. Rath, K. Schuler, and H. Stinlendorfer (*Annalen*, 1942, **553**, 103—146).—Benzoylation and phthaloylation of dinaphthylene dioxide (**I**) proceed relatively simply since only one mono- and only one di-derivative is produced in each case. Nitration is more complex since invariably two mono- and thence three di-derivatives arise which can only be separated chromatographically from one another. The reaction of 1 mol. of (**I**) with 2 mols. of BzCl and somewhat > 2 mols. of $AlCl_3$ in CS_2 or, more rapidly, in PhCl at 132° gives essentially 5 : 5′-dibenzoylnaphthylene dioxide (**II**), m.p. 324° (lit. 318°), with a small porportion of 5-*benzoylnaphthylene dioxide* (**III**), m.p. 252°. (**III**) is the main product when 1 mol. of BzCl is added gradually to a well-stirred mixture of somewhat > 1 mol. proportion of (**I**) and $AlCl_3$ in PhCl at 10—50°. The entry of >2 Bz is never observed even when a large excess of BzCl is used. (**II**) and Br vapour give essentially a Br_4-derivative, softens at 400°. (**II**) is much more resistant than (**I**) to oxidation and cannot be converted into a quinone by use of CrO_3 or Bz_2O_2. This does not immediately justify the assumption that Bz is attached to $C_{(4')}$ (Stinzendorfer, *Diss., Erlangen*, 1936). (**I**) is transformed by *o*-$C_6H_4Br{\cdot}COCl$ into *mono*-, m.p. 308°, and *di*-, m.p. 346°, -*o*-*bromobenzoylnaphthylene oxide*, which when boiled with quinoline and alkali pass respectively into 4 : 5-*benzoylenedinaphthylene dioxide*, m.p. 323°, and 5 : 4 : 5′ : 4′-*dibenzoylenedinaphthylene dioxide* (**IV**), from which a vat could not be obtained even in presence of C_5H_5N. The constitution of (**IV**) is established by its formation from *Bz*-2′-hydroxybenzanthrone, whereby also the attachment of Bz to $C_{(5)}$ in (**II**) and (**III**) is proved. *o*-$C_6H_4(CO)_2O$, (**I**), and $AlCl_3$ in boiling PhCl afford 5 : 5′-*di*-o-*carboxybenzoyldinaphthylene dioxide* (**V**), decomp. >330° (also +$2C_5H_5N$), converted by boiling Ac_2O into the corresponding *anhydride*, m.p. >330°, and by boiling HNO_3 (*d* 1·32) into a $(NO_2)_2$-derivative. Ring-closure of (**V**) or of the corresponding mono-derivative is greatly impeded by the pronounced tendency towards anhydride formation. H_2SO_4 causes sulphonation and oxidation in addition to the desired reaction, but (**V**) is transferred into 5 : 6 : 5′ : 6′-*diphthaloyldinaphthylene dioxide* (**VI**), decomp. 320—330° after darkening and softening, by boiling with P_2O_5 in BzCl–$C_6H_3Cl_3$. $POCl_3$ cannot replace P_2O_5 and the change does not occur with P_2O_5 in boiling $C_6H_3Cl_3$ in absence of BzCl. (**VI**) is a reddish-brown vat dye. Nitration of (**I**) is almost as easy as that of a phenol and mono-nitration is best effected by the action of 13% aq. HNO_3 on (**I**) in PhCl or $PhNO_2$. The product after removal of unchanged (**I**) cannot be separated into its components by crystallisation but is separated by chromatography over Al_2O_3 into violet 4- (**VII**), m.p. 324—325°, and red 6- (**VIII**), m.p. 313—315°, -*nitrodinaphthylene dioxide*. (**VII**) is reduced by granulated Sn and HCl to 4-*aminodinaphthylene dioxide* (**IX**) (*CHPh.* derivative, m.p. 236—238°), the *Ac*, m.p. 330° (decomp.) after darkening, and *Ac*$_2$ derivative, m.p. >250°, becomes brown at 260° and black at 350—360°, of which are obtained by addition of Zn dust to a suspension of (**VII**) in boiling Ac_2O–AcOH–C_5H_5N. (**VIII**) is similarly reduced to x-*aminodinaphthylene oxide*, which affords an *Ac*$_2$ compound, m.p. 258—259°, but could not be converted into a CHPh derivative. It could not be deaminated by 18% HCl under O_2 at 185°; this treatment transforms (**VII**) into 4 : 4′-dinaphthone dioxide, thus proving that NH_2 is attached to $C_{(4)}$ of (**IX**). Treatment of a suspension of finely-divided (**I**) in AcOH with 10% HNO_3 at 100° and chromatography of the product over Al_2O_3 leads to the isolation of raspberry-red (**X**), m.p. 310°, softens at 285°, brick-red (**XI**), m.p. >300° after darkening, and (in very small amount) violet (**XII**), m.p. >320° after darkening, *dinitrodinaphthylene dioxide*. (**X**) is reduced by granulated Sn and HCl to a *diamine* [red (*CHPh.*)$_2$ derivative, m.p. 291—292° (corr.); *diformyl* derivative, m.p. 345—346° (corr.)]. (**XI**) yields a brick-red *amine* [(*CHPh.*)$_2$ derivative, m.p. 314°; *triformyl* compound, decomp. >360°]. (**X**) and (**XI**) are also obtained from both (**VII**) and (**VIII**) whereas (**XII**) arises only from (**VII**) in 1—2% yield. (**X**) and (**XI**) can contain only 1 NO_2 at $C_{(4)}$ or $C_{(4')}$ whilst the other must be in that position which is already occupied in (**VIII**). (**X**) and (**XI**) do not contain the NO_2 groups in symmetrical positions. (**XII**) may be symmetrical and is then the 4 : 4′-compound; the minute amount available has prevented its attempted conversion into the 4 : 4′-quinone. (**X**) and (**XI**) are differentiated by the presence of the two NO_2 in the same nucleus in one case and in different nuclei in the other. Since there is no evidence of ring formation from the corresponding amines and PhCHO and HCO_2H it follows that $C_{(5)}$ and $C_{(5')}$ are not favoured for entry of the second NO_2. Only $C_{(6)}$ and $C_{(6')}$ remain and of these $C_{(6)}$ is preferred. 34% HNO_3 converts finely-divided (**I**) into *bi-nitrodinaphthylene dioxide*; the $(NO_2)_4$-compound, which decomposes at a very high temp., is obtained from (**I**) with cold, fuming HNO_3 or boiling 50% HNO_3 and the $(NO_2)_6$-derivative by very prolonged heating of (**I**) with HNO_3 (*d* 1·38).

[With A. Rieche and P. von Miller.] Dinaphthone dioxide (**XIII**) is transformed by boiling 50% HNO_3 into *dinitrodinaphthone dioxide* (**XIV**), decomp. at >360° without melting, which is reduced by $Na_2S_2O_4$ and NaOH in boiling H_2O to *diaminodinaphthone dioxide*; this does nor appear to give a simple Bz derivative with boiling BzCl. Cold nitrating acid converts (**I**) into *trinitrodinaphthone dioxide*, which gives a green product with NH_2Ph, red substances with $NPhMe_2$ and quinoline, and olive-green products with toluidine and xylidine. These reactions are not shown by (**XIV**). H. W.

Synthetic thiophan derivatives. E. R. Buchman and H. Cohen (*J. Amer. Chem. Soc.*, 1944, **66**, 847—848).—$CO_2Et{\cdot}CH_2{\cdot}S{\cdot}[CH_2]_2{\cdot}CO_2Et$ with Na in C_6H_6 gives Et 3-ketotetrahydrothiophen-4-carboxylate, b.p. 96°/4 mm. [phenylhydrazone, m.p. 100—101° (cf. Karrer *et al.*, A., 1944, II, 167); *semicarbazone*, m.p. 176°], converted by acid into *3-ketotetrahydrothiophen*, b.p. 83—85°/29 mm., unstable [*semicarbazone*, m.p. 196° (decomp.); 2 : 4-*dinitrophenylhydrazone*, m.p. 179° (decomp.)]. $CO_2Et{\cdot}CHMe{\cdot}S{\cdot}[CH_2]_2{\cdot}CO_2Et$ gives similarly *Et 3-keto-2-methyltetrahydrothiophen-4-carboxylate*, b.p. 93—95°/4·5 mm., and thence *3-keto-2-methyltetrahydrothiophen*, b.p. 82°/28 mm. (*semicarbazone*, m.p. 185—186°; *dinitrophenylhydrazone*, m.p. 161—162°). R. S. C.

Thiophan derivatives. R. B. Woodward and R. H. Eastman (*J. Amer. Chem. Soc.*, 1944, **66**, 849—850).—$SH{\cdot}CH_2{\cdot}CO_2Me$, $CH_2{:}CH{\cdot}CO_2Me$, and piperidine give $CO_2Me{\cdot}CH_2{\cdot}S{\cdot}[CH_2]_2{\cdot}CO_2Me$, converted by NaOMe in PhMe at 110° into, mainly, *Me 3-ketotetrahydrothiophen-4-carboxylate*, m.p. 37—38°, b.p. 128·5—129·5°/20 mm. [reddish-violet $FeCl_3$ colour; *semicarbazone*, m.p. 189·5—190°; *CHPh:*, m.p. 158—159°, and *furfurylidene* derivative (**I**), m.p. 157—158°], but in Et_2O at room temp. gives the *2-carboxylate* (**II**), b.p. 116—116·5°/9 mm. (*semicarbazone*, m.p. 187—187·5°; *CHPh:*, m.p. 129—130°, and *furfurylidene* derivative, m.p. 139·5—140°). Hydrolysis of either product gives *3-ketotetrahydrothiophen*, b.p. 58·2—58·4°/7 mm. [(*CHPh:*)$_2$, m.p. 187·5°, and *difurfurylidene* derivative, m.p. 191—192°]. With I or $FeCl_3$ etc., (**II**) gives a *compound*, $C_{12}H_{14}O_6S_2$, m.p. 188·5—189·5° [(*CHPh:*)$_2$ derivative, m.p. 236°], converted by desulphurisation into (?) δε-*dicarbomethoxy*-n-*octane*-γζ-*dione*, m.p. 125—126°, which with dil. acid yields (?) 2 : 5-*diethylfuran*-3 : 4-*dicarboxylic acid*, m.p. 152—153°. (**I**) contains the S–C skeleton of biotin. (Cf. preceding abstract.) R. S. C.

Thiophan compounds. V. P. Karrer, R. Keller, and E. Usteri (*Helv. Chim. Acta*, 1944, **27**, 237—246; cf. A., 1944, II, 167).—Thiophan derivatives are described containing $\cdot[CH_2]_4{\cdot}CN$ and $\cdot[CH_2]_4{\cdot}CO_2H$ attached to $C_{(2)}$. $Br{\cdot}[CH_2]_4{\cdot}CN$ and $CHNa(CO_2Et)_2$ in abs. EtOH at 50° give *Et$_2$ δ-cyano*-n-*butylmalonate*, b.p. 127—129°/0·01 mm. The corresponding *acid*, m.p. 116°, is transformed by Br in CCl_4–Et_2O at 20° into the non-cryst. *α-bromo-ε-cyanopentane-αα-dicarboxylic acid*, which passes at 100°/15 mm. into α-bromo-ε-cyanohexoic acid, which with CH_2N_2 in Et_2O affords the *Me* ester, b.p. 114—116°/0·02 mm. This is transformed by $SH{\cdot}[CH_2]_2{\cdot}CO_2Et$ and NaOEt in EtOH into *β-carbethoxyethyl ε-cyano-α-carbomethoxy*-n-*amyl sulphide*, b.p. 162—165°/0·01—0·02 mm., which with NaOEt in PhMe at 35° affords *Et 3-keto-2-δ-cyano*-n-*butylthiophan-4-carboxylate* (**I**), b.p. 153—155° (bath)/0·01—0·02 mm. (**I**) is converted by Br in CCl_4 at 0° into an unstable Br_1-derivative, which is gradually hydrolysed by boiling, dil. mineral acid and simultaneously oxidised by air to 3 : 4-*dihydroxy-2-δ-carboxy*-n-*butylthiophen*, m.p. 183°, which gives a dark blue colour with $FeCl_3$. (**I**) is hydrolysed and decarboxylated by a boiling mixture of dil. H_2SO_4 and AcOH to *3-keto-2-δ-carboxyl*-n-*butylthiophan* (**II**), m.p. 68°, which is more conveniently obtained by condensing $Br{\cdot}[CH_2]_4{\cdot}CO_2Et$ with $CHNa(CO_2Et)_2$ to *Et$_3$* n-*pentane-ααε-tricarboxylate*, b.p. 184°/15 mm.; this is hydrolysed to the *acid*, m.p. 88—89°, which yields successively the *α-Br*-derivative, decomp. 136—137°, non-cryst. α-bromopimelic acid, and *Et$_2$ α-bromopimelate*, b.p. 101—103°/0·005 mm. $SNa{\cdot}[CH_2]_2{\cdot}CO_2Et$ converts this compound into *β-carbethoxyethyl αε-dicarbethoxy*-n-*amyl sulphide*, b.p. 165—170°/0·02 mm., transformed by NaOEt in xylene into *3-keto-2-δ-carbethoxy*-n-*butylthiophan-4-carboxylate*, b.p. 148—155° (bath)/0·02 mm., converted by acid ketonic fission into (**II**). Passage of Br through a solution of (**II**) in MeOH kept acid to Congo-red by gradual addition of $CaCO_3$ gives *3-keto-4-hydroxy-2-δ-carboxy*-n-*butylthiophan*, m.p. 117—118° (*dioxime*, decomp. ~215° according to the rate of heating and size of crystal). (**I**) couples with p-$NO_2{\cdot}C_6H_4{\cdot}N_2Cl$ to *Et 4-p-nitrobenzeneazo-3-keto-2-δ-cyano*-n-*butylthiophan-4-carboxylate*, which, like the compound with p-$SO_3H{\cdot}C_6H_4{\cdot}N_2Cl$, could not be reduced to the 4-NH_2-compound. H. W.

Synthesis of 2 : 4-diarylthiophens. E. Campaigne (*J. Amer. Chem. Soc.*, 1944, **66**, 684—686).—"Anhydroacetophenone disulphide," CPhMe<S—CPh / S·CPhMe>CH (**I**) (modified prep.; cf. Baumann A., 1895, i, 362), m.p. 107—108°, at 180° gives a tar containing very small amounts of 2 : 4-diphenylthiophen (**II**), in boiling xylene gives an unsaturated, highly coloured mixture, but Cu chromite in boiling xylene gives 83% of (**II**), m.p. 120·6—121·5° [picrate, m.p. 133·1—133·6° (lit. 133—134°); 5-HgCl derivative, m.p. 222—223°]. p-$OMe{\cdot}C_6H_4{\cdot}COEt$, H_2S, and HCl in EtOH at 0° give "*anhydro*-p-*methoxypropiophenone disulphide*" [2 : 4 : 6-*tri*-p-*anisyl*-4-*methyl*-2-*ethyl*-1 : 3-*dithia*cyclo*hexane*] (53·5%), m.p. 158·1—158·6°, which in xylene gives a tar but no thiophen derivative, is unchanged in boiling EtOH alone or with Cu chromite, and with Cu chromite in boiling xylene gives 2 : 4-*di*-p-*anisyl*-3 : 5-*dimethylthiophen* (**III**) (66%), m.p. 112·3—112·8° (no derivatives formed). The reaction mechanism is thus: (**I**) → CSPhMe + $SH{\cdot}CPh{:}CH{\cdot}CPh{:}CH_2$ (**IV**); (**IV**) → (**II**) + H_2, Cu chromite or, less well, CSPhMe acting as H-acceptor. KOH in $(CH_2{\cdot}OH)_2$ at 225°/0·5 mm. hydrolyses (**III**) to 2 : 4-*di*-p-*hydroxyphenyl*-3 : 5-*dimethylthiophen* (61%), darkens 185°, m.p. 194—196° (*diacetate*, m.p. 125·9—126·9°). Absorption max. of (**II**) and (**III**) in MeOH are very similar (250, 265, and 280 mμ.), but ε differ notably. M.p. are corr. R. S. C.

Action of Grignard reagents on oximes. IV. Aliphatic Grignard reagents and mixed ketoximes. K. N. Campbell, B. K. Campbell, L. G. Hess, and I. J. Schaffner (*J. Org. Chem.*, 1944, **9**, 184—186).—Ethyleneimines are obtained from aliphatic Grignard reagents and aryl alkyl ketoximes best in PhMe at 95—100°; higher temp. cause excessive formation of tar. MgEtBr and $CPhMe{:}N{\cdot}OH$ give 2-*phenyl*-2-*ethylethyleneimine* (**I**), b.p. 85—86°/7 mm. (somewhat hygroscopic *hydrochloride*, m.p. 191—191·5°; *phenylthiocarbamide*, m.p. 99—100°; *α-naphthylcarbamide*, m.p. 129—130°), which does not reduce $KMnO_4$ in $COMe_2$ at room temp. It is hydrolysed by short boiling with 4N-HCl or 2N-H_2SO_4 to α-amino-β-phenylbutan-β-ol (**II**) and by longer boiling with 6N-HCl to $CHPhEt{\cdot}CHO$. (**I**) is obtained synthetically by successive action of $SOCl_2$ and KOH in EtOH on (**II**). Similarly $CPhMe{:}N{\cdot}OH$ and $MgPr^aBr$ afford 2-*phenyl*-2-n-*propylethyleneimine*, b.p. 90—91°/3 mm. (*hydrochloride*, m.p. 68—69°; *phenylthiocarbamide*, m.p. 100°), hydrolysed to *α-phenyl-α-aminomethyl*-n-*butyl alcohol*, b.p. 125—126°/7 mm. (*Bz* derivative, m.p. 112—113°), obtained also from $CH_2Bz{\cdot}NH_2$,HCl and $MgPr^aBr$. $CPhEt{:}N{\cdot}OH$ and MgEtBr afford 2-*phenyl*-3-*methyl*-2-*ethylethyleneimine*, b.p. 77—79°/3 mm. (*hydrochloride*, m.p. 158—159°; *phenylthiocarbamide*, m.p. 130—131°), hydrolysed by 2N-H_2SO_4 to $NH_2{\cdot}CHMe{\cdot}CPhEt{\cdot}OH$, b.p. 106—108°/5 mm. (*hydrochloride*, m.p. 230°; *Bz* derivative, m.p. 160°), obtained synthetically from $COPh{\cdot}CHMe{\cdot}NH_2$,HCl and MgEtBr. H. W.

Antispasmodics and anticonvulsants. III. Miscellaneous amides and esters. J. H. Billman and J. L. Rendall (*J. Amer. Chem. Soc.*, 1944, **66**, 745—746; cf. A., 1943, II, 262).—The following activities (W = weak; I = ineffective) as anticonvulsants and antispasmodics respectively are reported. $(CH_2Ph)_2CH{\cdot}CO{\cdot}O{\cdot}CH_2Ph$ (*W*, *I*), m.p. 81·5°; $CH_2Ph{\cdot}CHPh{\cdot}CO{\cdot}O{\cdot}CH_2Ph$ (*I*, *I*), b.p. 197—201°/1 mm.; CH_2Ph lævulate (—, *W*), b.p. 148—150°/3 mm.; *CH_2Ph 2-pyrrolidone-5-carboxylate* (*I*, *W*), b.p. 202—204°/2 mm.; *$NEt_2{\cdot}[CH_2]_2$ γ-diethylamino-α-phenyl*-n-*butyrate* (*I*, *I*), b.p. 170—173°/1 mm., *2-pyrrolidone-5-carboxylate* (*I*, *I*), b.p. 183—184°/3 mm., nicotinate (*I*, *I*), b.p. 130—132°/2 mm., and acetoacetate, b.p. 113°/2 mm.; benzyl- (—, *W*), m.p. 147·5°, and N-*benzyl*-N′-*triphenylmethyl-carbamide* (*W*, *I*), m.p. 228°; p-*dibenzylacetamido-benzophenone* (*I*, *I*), m.p. 60°, and *-acetophenone* (*W*, *I*), m.p. 135—136°. Preps. are by standard methods. R. S. C.

Magnesium *p*-2′ : 5′-dimethyl-1′-pyrrylphenyl bromide and [the corresponding] lithium [compound]. H. Gilman and G. J. O'Donnell (*J. Amer. Chem. Soc.*, 1944, **66**, 840).—Adding 1—2 drops of conc. HCl to p-$C_6H_4Br{\cdot}NH_2$ in hot $(CH_2Ac)_2$ gives p-bromo-2′ : 5′-dimethyl-1′-pyrrylbenzene (96%), m.p. 74°, which with Mg or, more readily, Li and then CO_2 gives p-2′ : 5′-dimethyl-1′-pyrrylbenzoic acid (72 and 80% yield, respectively), m.p. 196—197°. R. S. C.

Nitrogen compounds in petroleum distillates. XXV. Isolation and identification of 3- and 4-*cyclo*pentylpyridines from Californian petroleum. H. L. Lochte, E. D. Thomas, and P. Truitt (*J. Amer. Chem. Soc.*, 1944, **66**, 550—552; cf. A., 1943, II, 172).—When the aq. solution of the hydrochlorides of petroleum bases, b.p. 210—213°, is extracted with $CHCl_3$ (*loc. cit.*), the bases recovered from the aq. layer yield, by fractional distillation and fractional extraction, 3- (**I**), b.p. 215·5°/747 mm. (*picrate*, m.p. 117·5°), and 4-cyclopentylpyridine (**II**), b.p. 218°/744 mm. (*picrate*, m.p. 145—146°; *platinichloride*, decomp. 225—227°). Structures are proved by synthesis (cf. Emmert *et al.*, A., 1943, II, 384; Crouch *et al.*, A., 1943, II, 206). Adding $HgCl_2$–*cyclo*pentanone to $AlCl_3$ and a trace of I in C_5H_5N at the b.p. gives 1-2′-*pyridyl*cyclo*pentanol*, m.p. 83°, dehydrated by conc. H_2SO_4 at 100° to 1-2′-pyridyl-Δ^1-*cyclo*pentene, b.p. 238—239°/748 mm., whence H_2–PtO_2 in AcOH yields 2-*cyclo*pentylpyridine, b.p. 217—218°/750 mm. (*picrate*, m.p. 106·5°). Et_2 *cyclo*pentylmalonate (**III**), $CH_2{:}CH{\cdot}CN$, and NaOEt in dioxan at 35—40° and then 50° give *Et$_2$* cyclo*pentyl-β-cyanoethylmalonate* [*Et γ-cyano-α-carbethoxy-α*-cyclo*pentyl*-n-*butyrate*], b.p. 162°/10 mm., converted by boiling conc. HCl into α-cyclo*pentylglutaric acid* (**IV**), *form*, m.p. 69°, b.p. 176—177°/1·5 mm. The Na derivative of (**III**) with $Br{\cdot}[CH_2]_2{\cdot}CO_2Et$ in boiling xylene gives *Et$_2$ α-carbethoxy-α*-cyclo*pentylglutarate* (72%), b.p. 168—170°/2·4 mm., converted by boiling 10% aq. KOH into a *form*, m.p. 152·5°, of (**IV**). The *dichloride* (prep. by $SOCl_2$), b.p. 140—145°/4·5 mm., of (**IV**) (m.p. 69°) yields the *diamide*, m.p. 174° (evolution of NH_3), converted at 200°/5 mm. into the *imide* (**V**), m.p. 131°, also obtained from (**IV**) (m.p. 152·5°) by AcCl, followed by NH_3 and then heating. PCl_5

converts (V) at 43° (exothermally) and then 100° into 2 : 5 : 6-*trichloro*-3-cyclo*pentylpyridine*, m.p. 141°, which with H_2–Pd–C in MeOH at 20 lb. gives (I) (picrate, m.p. 118·7°). *cyclo*Pentanealdehyde, b.p. 136°, $CN{\cdot}CH_2{\cdot}CO{\cdot}NH_2$, and KOH in H_2O–EtOH give *αα'-dicyano-β-cyclopentylglutardiamide*, m.p. 213° (decomp.), hydrolysed by hot conc. HCl to *β-cyclopentylglutaric acid*, m.p. 111·5°; this is successively boiled with AcCl to give the anhydride, treated with NH_3 at 130°, heated at 210—230°, and treated with PCl_5 and finally H_2–Pd–C in MeOH, giving (II) (picrate, m.p. 146°). R. S. C.

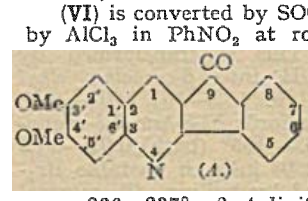
Pyridine acids etc.—See B., 1944, II, 198.

Behaviour of γ-keto- and aldehydo-acid derivatives at the dropping mercury electrode. II. Amides of *o*-benzoylbenzoic acid. S. Wawzonek, H. A. Laitinen, and S. J. Kwiatkowski (*J. Amer. Chem. Soc.*, 1944, **66**, 830—833).—Amides of o-$C_6H_3Bz{\cdot}CO_2H$ (I) are reduced polarographically in 0·1M-NBu_4I–50% dioxan, usually to the corresponding 1-keto-3-phenyl*iso*indole. The no. and position of the waves usually permit deductions as to the approx. amounts of cyclic and open-chain forms. o-$C_6H_4Bz{\cdot}CO{\cdot}NHPh$ (II), m.p. 195°, with $SOCl_2$ and then MeOH or with conc. HCl–MeOH at room temp. and then the b.p. gives 1-*keto*-3-*methoxy*-2 : 3-*diphenyl*-1 : 3-*dihydro*iso*indole*, m.p. 128—129° [regenerates (II) in conc. HCl–AcOH at room temp.], but the anil, m.p. 221°, gives the Me *n*-ester of (I). The ethylamide (III) of (I) similarly gives 1-*keto*-3-*methoxy*-3-*phenyl*-2-*ethyl*-1 : 3-*dihydro*iso*indole*, m.p. 73—75° (75—78°), which regenerates (III) in conc. HCl–AcOH. With $SOCl_2$–C_5H_5N and then NHPhMe–C_6H_6 at room temp. (I) gives the open-chain *methylanilide*, m.p. 144—146°. R. S. C.

Syntheses of quinolines from *o'*-aminobenzylidene-*p*-toluidines. W. Borsche and W. Ried [with, in part, J. Barthenheier] (*Annalen*, 1943, **554**, 269—290).—The synthesis of 6 : 7-dihydroxyquinoline is described and the limits of the synthesis of substituted quinolines from Schiff's bases and CO compounds are experimentally explored. o-$NH_2{\cdot}C_6H_4{\cdot}CHO$ is heated with $AcCO_2H$ in alkaline solution, which is then acidified and evaporated, thus giving quinoline-2-carboxylic acid in good yield. Similar treatment of a mixture of 6-aminoveratrylidene-*p*-toluidine (I) and $AcCO_2H$ leads to 6 : 7-*dimethoxyquinoline-2-carboxylic acid*, m.p. 215°, in 75% yield which diminishes to 60—65% when NaOH is absent or replaced by piperidine. The *picrate* has m.p. 215°. The acid is decarboxylated by Cu-bronze at 225°/high vac. to 6 : 7-*dimethoxyquinoline* (II), b.p. 135°/0·5 mm. [freely sol. *hydrochloride* and *sulphate*; *picrate*, m.p. 252°; *methiodide* (III), m.p. 258°], also obtained from (I), $CHMe{:}N{\cdot}OH$, and KOH in boiling EtOH. Determination of OMe in (II) according to Vieböck gives about half the expected val. probably because some of the MeI which is formed is involved in the production of methiodide and thus escapes volatilisation; in accordance with this hypothesis (III) evolves the amount of MeI required for 2 OMe. 6-Aminopiperonylidenetoluidine (IV) analogously affords 6 : 7-*methylenedioxyquinoline-2-carboxylic acid*, m.p. 231° (decomp.) (*picrate*, m.p. 182—183°), decarboxylated in a high vac. to 6 : 7-*methylenedioxyquinoline*, m.p. 116—117° (*picrate*, m.p. 245°). $CH_2Ph{\cdot}CO{\cdot}CO_2H$ behaves similarly to $AcCO_2H$. With (I) it gives 6 : 7-*dimethoxy*-3-*phenylquinoline-2-carboxylic acid*, m.p. 151—152°, decarboxylated to 6 : 7-*dimethoxy*-3-*phenylquinoline*, m.p. 90—91°, and with (IV) it yields 6 : 7-*methylenedioxy*-3-*phenylquinoline-2-carboxylic acid*, m.p. 172° (decomp.), and thence 6 : 7-*methylenedioxy*-3-*phenylquinoline*, m.p. 132°. *o'*-Aminobenzylidene-*p*-toluidine (V) with $CH_2Ac{\cdot}CO{\cdot}CO_2Et$ yields *Et* 3-*acetylquinoline-2-carboxylate*, m.p. 93—94°, which does not give a picrate or a 2 : 4-dinitrophenylhydrazone but is transformed by $N_2H_4.H_2O$ in boiling EtOH into 4 : 5-2' : 3'-*quinolinopyridazinone*, decomp. >320°. Similarly (I) gives *Et* 6 : 7-*dimethoxy*-3-*acetylquinoline-2-carboxylate*, m.p. 187—188°, converted into 6-*keto*-3-*methyl*-4 : 5-2' : 3'-(6' : 7'-*dimethoxyquinolino*)-1 : 6-*dihydropyridazine*, m.p. ~315°, darkens at 295°. 6 : 7-*Dimethoxy*-3-*acetylquinoline-2-carboxylic acid*, m.p. 194° (decomp.), is decarboxylated to 6 : 7-*dimethoxy*-3-*acetylquinoline*, m.p. 161—162° (2 : 4-*dinitrophenylhydrazone*, m.p. 301°). Analogously, (IV) gives *Et* 6 : 7-*methylenedioxy*-3-*acetylquinoline-2-carboxylate*, m.p. 160—161° (corresponding *pyridazinone*, m.p. 355—357°). $CH_2Bz{\cdot}CO{\cdot}CO_2Et$ behaves similarly, giving with (V) *Et* 3-*benzoylquinoline-2-carboxylate*, m.p. 89° (6-*keto*-3-*phenyl*-4 : 5-2 : 3-*quinolino*-1 : 6-*dihydropyridazine*, m.p. 308—310°), with (I) *Et* 6 : 7-*dimethoxy*-3-*benzoylquinoline-2-carboxylate*, m.p. 196—197° (6-*keto*-3-*phenyl*-4 : 5-2' : 3'-6' : 7'-*dimethoxyquinolino*-1 : 6-*dihydropyridazine*, m.p. 316—318°), hydrolysed to 6 : 7-*dimethoxy*-3-*benzoylquinoline-2-carboxylic acid*, m.p. 206—207°, decarboxylated to 6 : 7-*dimethoxy*-3-*benzoylquinoline*, m.p. 156—157°, and with (IV) *Et* 6 : 7-*methylenedioxy*-3-*benzoylquinoline-2-carboxylate*, m.p. 247—248°. (V) does not yield the desired 2-acylquinolines or other well-defined products with *αβ*-diketones $COR{\cdot}COMe$ or with $COMe{\cdot}CPh{:}N{\cdot}OH$. With $COMe{\cdot}CH{:}N{\cdot}OH$ (V) affords mainly quinoline-2-aldoxime, m.p. 188—189° (*picrate*, m.p. 226—227°), and an unidentified substance, m.p. 226—227°, insol. in alkali. Similarly, (I) gives 6 : 7-*dimethoxyquinoline-2-aldoxime*, m.p. 243° (*picrate*, m.p. 253—254°; a methiodide could not be prepared), and an alkali-insol. *by-product*, $C_{32}H_{34}O_5N_4$, m.p. 267—269° (*Ac* derivative, m.p. 176—177°; 2 : 4-*dinitrophenylhydrazone*, m.p. 275—276°), which could not be identified. (V) likewise affords 6 : 7-*methylenedioxyquinoline-2-aldoxime*, m.p. 252—253° (*picrate*, vigorous decomp. >340°), and an alkali-insol. *substance*, $C_{14}H_{10}O_3N_2$, m.p. >365°. $COMe{\cdot}CH{:}N{\cdot}NHPh$ and (V) in presence of piperidine at 160—170° appear to give the *anil*, o-$C_6H_4Me{\cdot}N{:}CH{\cdot}C_6H_4{\cdot}N{:}CMe{\cdot}CH{:}N{\cdot}NHPh$, m.p. 221° (quinoline-2-aldehydephenylhydrazone has m.p. 203°), which could not be distilled without complete decomp. and is indifferent towards boiling Ac_2O and KOH–EtOH. Analogously constituted *compounds*, m.p. 151—152° and 173—174° respectively, are derived from (I) and (IV). αγ-Diketones and β-CO-esters with the group Ac react readily in all cases. Thus (V) and CH_2Ac_2 give 3-acetyl-2-methylquinoline, m.p. 57—58° (*picrate*, m.p. 233—234° after darkening; 2 : 4-*dinitrophenylhydrazone*, m.p. 216—217°). 6 : 7-*Dimethoxy*-3-*acetyl*-2-*methylquinoline*, m.p. 142—143° (*picrate*, m.p. 265—266°), and 6 : 7-*methylenedioxy*-3-*acetyl*-2-*methylquinoline*, m.p. 171—172° (*picrate*, m.p. 234—236°), are derived similarly from (I) and (IV) respectively. A 2 : 4-dinitrophenylhydrazone could not be obtained from 6 : 7-*dimethoxy*-3-*benzoyl*-2-*methylquinoline*, m.p. 158°, very smoothly prepared from CH_2AcBz and (I) in presence of piperidine at 100°. CH_2Ac_2 is transformed by a boiling solution of 2 : 4-$(NO_2)_2C_6H_3{\cdot}NH{\cdot}NH_2$ into 1-2' : 4'-*dinitrophenyl*-3 : 5-*dimethylpyrazole*, m.p. 119—120°; CH_2AcBz similarly yields 5-*phenyl*-1-2' : 4'-*dinitrophenyl*-5-*methylpyrazole*, m.p. 128—129°. $CH_2Bz{\cdot}CO_2Et$ and (V) afford the non-cryst. *Et* 2-*phenylquinoline*-3-*carboxylate* (*picrate*, m.p. 159—160°), hydrolysed to the acid, m.p. 229°. Similarly (I) gives *Et* 6 : 7-*dimethoxy*-2-*phenylquinoline*-3-*carboxylate*, m.p. 155° [*acid* (VI), m.p. 238—239° (decomp.)], and (IV) yields *Et* 6 : 7-*methylenedioxy*-2-*phenylquinoline*-3-*carboxylate*, m.p. 149°, hydrolysed to the *acid* (VII), m.p. 283—284° (with formation of 6 : 7-methylenedioxy-2-phenylquinoline, m.p. 110°). (V) and Ac_2O alone or in presence of Et_2O at room temp. yield *o'-acetamidobenzylidene*-p-*toluidine*, m.p. 148—149°, which is deacetylated but does not give carbostyril under the influence of alkali. Under the same conditions (I) is transformed directly into 2-*hydroxy*-6 : 7-*dimethoxyquinoline*, m.p. 179° (with some p-$C_6H_4Me{\cdot}NHAc$, m.p. 150—152°), and (IV) into 2-*hydroxy*-6 : 7-*methylenedioxyquinoline*, m.p. 158—159°.

Treatment of (II) with boiling AcOH–HI (*d* 1·7) leads to 6 : 7-*dihydroxyquinoline hydriodide*, converted by aq. H_2SO_4 into the corresponding *sulphate*, m.p. ~270°, darkens at 240°; this is transformed by $NaHCO_3$ into the *Na*$_1$ compound, m.p. >360°, slowly darkens >225°, of 6 : 7-dihydroxyquinoline (VIII), which gives (Schotten–Baumann) 6 : 7-*dibenzoyloxyquinoline*, m.p. 135—136°; (VIII) affords a *picrate*, m.p. 270°. (II) is demethylated by pyridinium chloride at 180—190° to (VIII), m.p. 248—250°, softens at 230° (also +2H$_2$O), isolated by pptn. of the Pb salt, which is treated with H_2S. 6 : 7-*Dimethoxy*-2-*methylquinoline* (+2H_2O), m.p. 285°, becomes discoloured at 240°, and softens at ~265°, is obtained similarly.

(VI) is converted by $SOCl_2$ into the *chloride*, m.p. 225°, cyclised by $AlCl_3$ in $PhNO_2$ at room temp. into 3' : 4'-*dimethoxybenz*-1' : 6'-2 : 3-4-*azafluorenone* (*A*), m.p. 290—295° (2 : 4-*dinitrophenylhydrazone*, m.p. 315—316°). Analogously, 6 : 7-methylenedioxy-3-phenylquinoline-2-carboxyl chloride gives 3' : 4'-*methylenedioxybenz*-1' : 6'-2 : 3-1-*azafluorenone*, m.p. 276—277° (*oxime*, m.p. 236—237°; 2 : 4-*dinitrophenylhydrazone*, decomp. 332°), and the chloride of (VII) is cyclised to 3' : 4'-*methylenedioxybenz*-1' : 6'-2 : 3-4-*azafluorenone*, m.p. 245—246° (*oxime*, m.p. 330°; 2 : 4-*dinitrophenylhydrazone*, blackens >320°, m.p. >360°). Quinoline-2-aldoxime is converted by boiling Ac_2O into 2-cyanoquinoline, m.p. 93°, from which a picrate or methiodide could not be obtained. The oxime is transformed by $NHPh{\cdot}NH_2$ and conc. HCl in boiling EtOH into quinoline-2-aldehydephenylhydrazone, m.p. 203—204° (*hydrochloride*, m.p. 277—278°). Attempts to obtain quinoline-2-aldehyde by treatment of the oxime with CH_2O, o-$C_6H_4(CO)_2O$, or dil. H_2SO_4 were unsuccessful. The *oxime sulphate* has m.p. 203—204°. Analogous methods lead to 6 : 7-*dimethoxyquinoline-2-nitrile*, m.p. 232—233°, and -2-*aldehydephenylhydrazone*, m.p. 170° (*hydrochloride*, m.p. 257—258°), and to 6 : 7-*methylenedioxyquinoline-2-nitrile*, m.p. 253—254°, and -2-*aldehydephenylhydrazone*, m.p. 245—246° (*hydrochloride*, m.p. 299—300°). W



Quinolines patterned as " open models " of atabrine. H. Gilman and S. M. Spatz (*J. Amer. Chem. Soc.*, 1944, **66**, 621—625). *m*-$C_6H_4Cl{\cdot}Li$ (I) {prep. from *m*-C_6H_4ClBr and $LiBu^n$ in Et_2O–N_2 at —35° [for, best (69·7%), 9 min.]} with 6-methoxyquinoline in Et_2O–N_2 at, best, 0° gives, after hydrolysis, 6-*methoxy*-2-m-*chlorophenylquinoline* (49·3—53%), m.p. 110—111° (*picrate*, m.p. 190—197°), converted by BzO_2H in $CHCl_3$ at 0° into the N-*oxide* (73%), m.p. 153—154° (*picrate*, m.p. 158·5—159°), which with $POCl_3$ at 100° and then the b.p. gives 4-*chloro*-6-*methoxy*-2-m-*chlorophenylquinoline* (II) (63·2—63·8%), m.p. 153—154°. (II) is also obtained from 4-chloro-6-methoxyquinoline and (I) in 34·7% yield and with $NEt_2{\cdot}[CH_2]_3{\cdot}CHMe{\cdot}NH_2$ at 200—205° gives 4-δ-*diethylamino*-α-*methyl*-n-*butylamino*-6-*methoxy*-2-m-*chlorophenylquinoline* (III) (60·7%), amorphous. 6-*Methoxy*-, m.p. 194—195° (*picrate*, m.p. 205°; N-*oxide*, m.p. 166—168°), 4-*chloro*-6-*methoxy*-, m.p. 163·5—164°, and 4-δ-*diethylamino*-α-*methyl*-n-*butylamino*-6-*methoxy*- (IV), amorphous,

-2-p-*chlorophenylquinoline* are similarly prepared. *o*-OMe·C_6H_4Li and quinoline lead similarly to 2-*o*-*anisyl*-, b.p. 201—204° (203·5°)/2 mm. [*hydrochloride*, m.p. 184·5—185° (decomp.); *picrate*, m.p. 177—178°; N-*oxide*, m.p. 178—178·5° (*picrate*, m.p. 133·5—134°)], 4-*chloro*-2-*o*-*anisyl*-, m.p. 96—98° (*picrate*, m.p. 200—201°), 4-δ-*diethylamino*-α-*methyl*-n-*butylamino*-2-*o*-*anisyl*-*quinoline* (**V**), b.p. 248—255°/0·025 mm. Similar reactions lead to 6-methoxy- (N-*oxide*, m.p. 170—171°), 4-chloro-6-methoxy-, m.p. 110—111°, and 4-δ-*diethylamino*-α-*methyl*-n-*butylamino*-6-*methoxy*-2-*phenylquinoline* (**VI**), amorphous. (**III**), (**IV**), and (**VI**), but not (**V**), show antimalarial activity. R. S. C.

Arylation of *iso*quinoline derivatives. II. Synthesis of 1-*m*-nitrophenyl-3 : 4-dihydro*iso*quinoline, 1-*o*-nitrophenyl-3 : 4-dihydro*iso*quinoline, and their derivatives. V. M. Rodionov and E. V. Javorskaja (*J. Gen. Chem. Russ.*, 1943, **13**, 491—496).—The object of the work was the prep. of *iso*quinoline antimalarials. Ph·$[CH_2]_2$·NH_2 with *m*-NO_2·C_6H_4·COCl gave m-*nitrobenz*-β-*phenylethylamide*, m.p. 119—120° (62% yield), which with P_2O_5 in boiling xylene gave 1-m-*nitrophenyl*-3 : 4-*dihydroisoquinoline* (64%), m.p. 51—52° (*hydrochloride*, m.p. 213—214°), reduced by Fe–AcOH to the m-NH_2-compound (**I**) (71%), m.p. 119—120° [*hydrochloride*, m.p. 280—281° (decomp.); *Ac* derivative (69%), m.p. 114—117°], is reduced by Sn–HCl to 1-m-*aminophenyl*-1 : 2 : 3 : 4-*tetrahydroisoquinoline* (78%), m.p. 126—127°. NEt_2·$[CH_2]_3$·Cl and (**I**) gave 3-γ-*diethylaminopropylamino*-1-*phenyl*-3 : 4-*dihydroisoquinoline* (**II**) (48%), m.p. 226—229° (*hydrochloride*, hygroscopic, m.p. indef.). Ph·$[CH_2]_2$·NH_2 with *o*-NO_2·C_6H_4·COCl gave o-*nitrobenz*-β-*phenylethylamide* (65%), m.p. 115—116°, which with P_2O_5 in boiling xylene gave 1-*o*-*nitrophenyl*-3 : 4-*dihydroisoquinoline* (73%), m.p. 84—85° (*hydrochloride*, m.p. 211—213°), reduced (Fe–AcOH) to the o-NH_2-compound (52%), m.p. 95—96° (*Ac* derivative), which was reduced (Sn, aq.-alcoholic HCl) to 1-*o*-*aminophenyl*-1 : 2 : 3 : 4-*tetrahydroisoquinoline* (82%), m.p. 108—109°, and with NEt_2·$[CH_2]_3$·Cl gave 1-*o*-γ-diethylaminopropylaminophenyl-3 : 4-dihydro*iso*quinoline (III) (47%), m.p. 215—219°. (**II**), (**III**), and 1-p-γ-*diethylaminopropylaminophenyl*-3 : 4-*dihydroisoquinoline* (*ibid.*, 1941, **11**, 446) were inactive as avian antimalarials. F. Hi.

Hydantoins of sulphur-containing amino-acids. J. V. Karabinos and J. L. Szabo (*J. Amer. Chem. Soc.*, 1944, **66**, 649—650).—Syntheses are effected following the discovery that the hydantoin ring is unaffected by Na in liquid NH_3. Thus Na converts *l*-cystine hydantoin (**I**) in NH_3 into l-*cysteine hydantoin* (**II**), m.p. 144—145° (cf. Boyd, A., 1934, 195). *S*-Benzylhomocysteine in hot aq. KCNO and then hot HCl gives the *hydantoin*, m.p. 103—104°, whence Na–NH_3 yields dl-*homocysteine hydantoin* (**III**), m.p. 121—122°. Homocystine with KCNO and then HCl similarly yields *homocystine hydantoin* (**IV**), m.p. 204—205°, and thence (**III**). I oxidises (**II**) to (**I**) or (**IV**) to (**III**). M.p. are taken on a microscope stage. R. S. C.

Dehydration of hydantoin-5-propionic acid. J. L. Szabo and J. V. Karabinos (*J. Amer. Chem. Soc.*, 1944, **66**, 650—651).—Hydantoin-5-propionic acid, m.p. 170°, with P_2O_5 in boiling xylene gives the *hydantoin-5-propio*-1-*lactam*, NH$<$CO·N—CO$>$$CH_2$ / CO·CH·CH_2 (**I**) (78%), m.p. 201°, and with boiling Ac_2O gives the *Ac* derivative (88%), m.p. 147—148°, of (**I**), also obtained from (**I**) by Ac_2O. The structure of (**I**) follows by analogy from conversion of 2-thiohydantoin-5-propio-1-lactam (prep. from 2-pyrrolidone-5-carboxylic acid and NH_4CNS in AcOH–Ac_2O at 100°) by hydrolysis by boiling N-HCl into 2-thiohydantoin-5-propionic acid and recovery therefrom by P_2O_5 in boiling PhMe. R. S. C.

Double invert soaps : symmetrical dipiperidinium salts. J. B. Niederl and A. E. Lanzilotti (*J. Amer. Chem. Soc.*, 1944, **66**, 844—845).—By AlkBr in hot 95% EtOH are prepared *methylenebis*-1-*piperidinium di*-n-*heptyl*, m.p. 178°, -n-*octyl*, m.p. 162°, -n-*tetradecyl*, m.p. 183°, and -n-*hexadecyl dibromide*, m.p. 176°, and *benzylidenebis*-1-*piperidinium di*-n-*heptyl*, m.p. 177°, -n-*octyl*, m.p. 165°, -n-*tetradecyl*, m.p. 181°, and -n-*octadecyl dibromide*, m.p. 179°. R. S. C.

Sulphanilamidopolyalkylpyrimidines.—See B., 1944, III, 142.

Amides of nicotinic and related acids. II. J. H. Billman and J. L. Rendall (*J. Amer. Chem. Soc.*, 1944, **66**, 540—541; cf. A., 1943, II, 262).—The following are prepared, usually by heating the appropriate acid and (high-boiling) amine in xylene with continuous removal of H_2O or from the ester and amine: *nicotin-benzyl*- (**I**), m.p. 72—73°, -n-*amyl*-, b.p. 170—171°/1 mm., -*allyl*-, b.p. 158—161°/1 mm., and -*dibutylaminopropyl-amide*, b.p. 226—230°/2 mm.; *pyridine*-4-*carboxyl-benzyl*-, m.p. 84·5—85°, -n-*amyl*-, b.p. 158—159°/2 mm., -*allyl*-, b.p. 158—159°/2 mm., and -*dibutylaminopropyl-amide*, b.p. 236—240°/2 mm.; *pyridine*-2-*carboxyl-benzyl*-, m.p. 87—87·5°, -n-*amyl*-, b.p. 135—138°/2 mm., -*allyl*-, b.p. 166—170°/2 mm., and -*dibutylaminopropyl-amide*, b.p. 209—212°/1 mm.; *pyrazinecarboxyl*-, m.p. 116°, and *quinoline*-3-*carboxyl-benzylamide*, m.p. 139—139·5°; *pyrazine*-2 : 3-*di*(*carboxyl-benzyl*-, m.p. 171—171·5°, and -n-*amyl-amide*), m.p. 145·5—146°. Quinoxaline is prepared from *o*-$C_6H_4(NH_2)_2$ (27·0) and (OH·CH·$SO_3H)_2$ (68·8 g.) in (<700 ml.). (**I**) has antispasmodic activity. R. S. C.

Quinoxaline formation and the ortho-effect. Influence of bromine atoms and nitro-groups. R. C. Fuson and Q. F. Soper (*J. Org. Chem.*, 1944, **9**, 193—200).—Quinoxaline formation is made possible by the introduction of Br or NO_2 into the mesityl ring of mesitylglyoxal or Ph mesityl diketone. In the latter compound the effect persists even when the substituent is on the Ph ring. Arylglyoxals which are not sufficiently reactive to yield quinoxalines always form Schiff's bases. Benzils, on the other hand, always form quinoxalines if they react at all. Substitution of Br or NO_2 on either aromatic nucleus of a benzil enhances its tendency to undergo reaction with *o*-$C_6H_4(NH_2)_2$. The H-bonding theory alone does not provide an adequate explanation of these observations. Most of the following $(CO)_2$-compounds are obtained by oxidising the ketone with a small excess of SeO_2 in boiling, wet dioxan: 3-*nitromesityl*- (**I**), m.p. 217—218·5° (corr.), 2 : 4 : 6-*triisopropylphenyl*- (**II**), b.p. 129—135°/4·5 mm. [*phenylhydrazone*, m.p. 158·5—159·5° (corr.); *semicarbazone*, m.p. 179—180° (corr.); *hydrazone*, m.p. 153—154° (decomp.)], 3-bromomesityl- (**III**), (2 : 4-*dinitrophenylhydrazone*, m.p. 203—205°), and 3-bromo-5-nitromesityl-glyoxal (**IV**) (2 : 4-*dinitrophenylhydrazone*, m.p. 260—261°), *mesityl Me*, b.p. 138—139°/17 mm., p-*nitrophenyl mesityl*, m.p. 115—116° (corr.), m-*nitrophenyl mesityl*, m.p. 108—108·5° (corr.), and p-*bromophenyl mesityl diketone*, m.p. 102—103° p-, m.p. 211—211·5° (corr.), and m-*nitrophenylmesityl*-, m.p. 144—146°, *phenyl*-3′-*nitromesityl*-, m.p. 151—152° (corr.), 4′-*nitrophenyl*-3′′-*nitromesityl*-, m.p. 198—199° (corr.), 3′-*nitrophenyl*-3′′ : 5′′-*dinitromesityl*-, m.p. 188—189° (corr.), *phenyl*-3′ : o′-*dibromomesityl*-, m.p. 187—188°, 4′-*bromophenylmesityl*-, m.p. 190—191°, *di*-*o*-*tolyl*-, m.p. 132—133°, and *nitrodi*-*o*-*tolyl*-*quinoxaline*, m.p. 197·5—198·5°, are described. Acetomesitylene is converted by HNO_3 (*d* 1·51), AcOH, and Ac_2O into 3-*nitroacetomesitylene*, b.p. 157—159°/8 mm., m.p. 23°, which does not give an oxime. 2 : 4 : 6-Triisopropylphenylglyoxal is converted by fuming HNO_3 and glacial AcOH into 3 : 5-*dinitro*-2 : 4 : 6-*triisopropylphenylglyoxylic acid*, m.p. 90—92°, which does not react with 2 : 4-$(NO_2)_2C_6H_2$·NH·NH_2. 3 : 5-*Dinitro*-2 : 4 : 6-*triisopropylacetophenone*, m.p. 144—145°, and 3-*nitrophenyl* 3′ : 5′-*dinitromesityl diketone*, m.p. 184—185° (corr.), are obtained from the parent ketone and fuming HNO_3. *Ph* 3-*nitromesityl diketone*, m.p. 89·5—90·5°, from COPh·CO·$C_6H_2Me_3$, fuming HNO_3, AcOH, and Ac_2O at room temp., is oxidised by H_2O_2 in boiling dioxan to BzOH and 3-nitromesitoic acid. *p*-NO_2·C_6H_4·CH_2·COCl, *s*-$C_6H_3Me_3$, and $AlCl_3$ in CS_2 afford p-*nitrobenzyl mesityl ketone*, m.p. 96—97° (corr.). m-*Nitrobenzyl mesityl ketone*, m.p. 133·5—134·5° (corr.), is obtained analogously. Nitration of the diketone leads to 4-*nitrophenyl* 3′-*nitromesityl diketone*, m.p. 99·5—101° (corr.). 3 : 5-Dibromo-2 : 4 : 6-trimethylbenzoin is oxidised by $CuSO_4$ in aq. C_5H_5N to Ph 3 : 5-dibromomesityl diketone, m.p. 101—104°. *s*-$C_6H_3Me_3$, *p*-C_6H_4Br·CH_2·COCl, and $AlCl_3$ in CS_2 give p-*bromobenzyl mesityl ketone*, m.p. 82—83°. Mesitil and fuming HNO_3 produce 3 : 3′ : 5 : 5′-*tetranitromesitil*, m.p. 317—319° (decomp.), which does not react with *o*-$C_6H_4(NH_2)_2$. A similar behaviour is shown by 3-*nitrophenyl* 3′ : 5′-*dinitro*-2′ : 4′ : 6′-*triisopropylphenyl diketone*, m.p. 166—167°, and 4 : 4′-dimethoxy-2 : 6-xylil. (**I**), (**II**), and (**III**) with *o*-$C_6H_4(NH_2)_2$ give Schiff's *bases*, $C_{28}H_{26}O_5N_4$, $C_{40}H_{50}O_2N_2$, and $C_{28}H_{26}O_2N_2Br_2$, m.p. 258—258·5° (corr.), 173—174°, and 165—167° or 202° (softens at 177° when slowly heated), whereas (**IV**) appears to yield a *quinoxaline*, $C_{17}H_{14}O_2N_3Br$, m.p. 156—157° (decomp.). H. W.

Structure of indanthrone, indigo, and some of their derivatives. R. Gill and H. I. Stonehill (*J. Soc. Dyers and Col.*, 1944, **60**, 183—186).—The relation in the properties of indigo and indanthrone is explained by assigning H-bonded formulæ, which are resonance hybrids of the keto- and enol forms; this is supported by the different properties of *N*-methylindanthrone, which cannot form a H-bonded structure. H. A. P.

Gliotoxin, the antibiotic principle of *Gliocladium fimbriatum*. II. General chemical behaviour and crystalline derivatives. W. F. Bruce, J. D. Dutcher, J. R. Johnson, and L. M. Miller. **Structure of gliotoxin : (III) degradation by hydriodic acid; (IV) action of selenium.** J. D. Dutcher, J. R. Johnson, and W. F. Bruce (*J. Amer. Chem. Soc.*, 1944, **66**, 614—616, 617—619, 619—621; cf. A., 1944, II, 116).—II. In boiling 10% NaOH, gliotoxin (**I**) gives NH_2Me, H_2S (40—60%), S (a little), and a red, amorphous, alkali-sol. substance containing N and S. In boiling 15% $Ba(OH)_2$ it gives a cryst. product, whence sublimation yields a little indole-2-carboxylic acid (**II**). (**I**) is inert towards PhNCO, and with CH_2N_2, MeI, or Me_2SO_4 gives gums. It gives no reactions for OMe or OEt, CO, CH_2O_2, or CH_2S_2. It reacts with $AgNO_3$–NH_3, Folin's reagent, or nitroprusside, probably owing to liberation of S″ by the alkali. $KMnO_4$, aq. Br, or NaOCl yields SO_4″. Na_2SO_3, $SnCl_2$, HI, Al–Hg, Zn– or Sn–acid gives H_2S. $Hg(OAc)_2$ or $AgNO_3$ liberates only 1 atom of S. $CuSO_4$, $Pb(OAc)_2$, or $BaCl_2$ has no effect. In C_5H_5N, (**I**) shows 2—3 active H ($MgEtBr$); with boiling Ac_2O or BzCl it gives gums, but at room temp. yields a *di*-p-*bromo*-, m.p. 193° (decomp.), $[\alpha]_D$ +20° in $CHCl_3$, and *di*-p-*nitro-benzoate*, m.p. 189° (decomp.), $[\alpha]_D^{22}$ +13° in $CHCl_3$, but no reaction occurs with *p*-C_6H_4Me·SO_2Cl or *o*-$C_6H_4(CO)_2O$–C_5N_5N. (**I**) thus contains an indole nucleus.

III. With red P and HI in boiling AcOH, (**I**) gives 1 : 4-*diketo*-

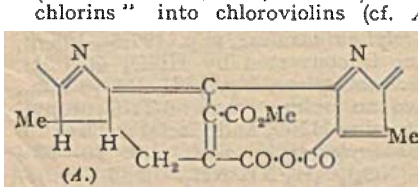
2 : 3-*dimethyltetrahydropyrazino*[1, 2a]*indole* [3 : 6-*diketo*-1 : 2-*dimethylindolo*-1′ : 2′-4 : 5-*tetrahydropyrazine*] (**III**), m.p. 122°, 2 H_2S, and 2 H_2O. The structure of (**III**) is proved by synthesis and by hydrolysis by 0·5N-KOH–MeOH at room temp. to N-*indole*-2-*carboxyl*-N-*methylalanine* (**IV**), m.p. 187° [Et ester (**V**), m.p. 127°], whence boiling 20% aq. KOH–N_2 yields (**II**). The chloride (prep. by $SOCl_2$–Et_2O) of (**II**) and *dl*-NHMe·CHMe·CO_2Et in Et_2O gives (**V**) (m.p. 126°), whence hydrolysis yields (**IV**) and cyclisation by 1% HCl–EtOH at room temp. yields (**III**). (**III**) is also obtained if synthetic (**V**) (probably containing a trace of HCl) is kept in EtOH.

IV. Se and (**I**) at 230—250° give 1 : 3 : 4-*triketo*-2-*methyltetrahydropyrazino*[1, 2a]*indole* [2 : 3 : 6-*triketo*-1-*methylindolo*-1′ : 2′-4 : 5-*tetrahydropyrazine*] (**VI**), m.p. 253—255°, 2H_2S, H_2O, and a derivative from 1 C. In N-KOH–MeOH at room temp., (**VI**) consumed 2 KOH, giving *indole*-2-*carboxylmethylamide* (**VII**), m.p. 220° [*picrate*, m.p. 168—170° (decomp.); *I*-derivative, m.p. 186°, prepared by aq. I–KI–NaOH] (and ? $H_2C_2O_4$), whence boiling 25% aq. KOH–N_2 yields (**II**) and NH_2Me. The chloride of (**II**) and NH_2Me in C_6H_6 give (**VII**), which with COCl·CO_2Et in C_5H_5N–Et_2O at room temp. gives (**VI**), m.p. 255°. R. S. C.

Nuclear acylations according to Friedel–Crafts.—See A., 1944, II, 297.

1 : 3 : 5-Triazines.—See B., 1944, II, 198.

Chlorophyll. CXV. Chloroviolins. M. Strell and E. Iscimenler (*Annalen*, 1942, **553**, 53—66).—The conversion of "unstable chlorins" into chloroviolins (cf. *A*) is described. "Unstable chlorin 7" Me_1 ester (**I**) is converted by BzCl in C_5H_5N into *chloroviolin* Me_1 *ester* (**II**), m.p. >330° (*Cu* compound, m.p. >320°), which is not (*A*), sol. in alkali. Fractionation of (**II**) with 18% HCl and esterification of the alkali-sol. portion leads to *chloroviolin* Me_3 *ester* (**III**), gradual decomp. >270°. Cold, dil. KOH–MeOH also causes fission of (**II**), but prolonged action causes profound decomp. The removal of H_2O by BzCl appears mainly catalytic and is sp.; AcCl, $PhSO_2Cl$, BzCN, and NH_2Bz have no effect and BzBr is somewhat less efficient. The spectra of the chloroviolins are closely similar to those of the neopurpurins. (**III**) may also be regarded as neopurpurin 6 Me_3 ester. In addition to (**II**), an amorphous compound with chlorin spectrum is also obtained from (**I**) particularly when impure C_5H_5N is used. Phæoporphyrin a_7 lactone appears to be benzoylated by BzCl in C_5H_5N; the chloroviolin reaction appears confined to the chlorin system. "Unstable chlorin 7" Me_2 ester does not show the change, which is undergone by "unstable chlorin 7" if reaction is rapid. The reaction is also negative with pyrrochlorin-7-glycollic acid and "unstable chlorin 5." "Unstable mesochlorin 7 Me_1 ester" gives *mesochloroviolin* Me_1 *ester* (**IV**), m.p. 292°, $[\alpha]_{20}$ −343°, and Me_3 ester (**V**), m.p. 198°, $[\alpha]^{20}$ −495° (with filter), −990° (violet colour, without filter), which yield *salts*, $C_{35}H_{32}O_5N_4Cu$, m.p. >310°, $[\alpha]^{20}$ +396° (with filter), +992° (without filter, green colour), and $C_{37}H_{38}O_6N_4Zn$, m.p. 218°, respectively. Important support for the assumption of a neopurpurin-like structure is found in the conversion of (**IV**) or (**V**) by HI into *chloroviolinporphyrin* Me_3 ester, m.p. 278° (*Cu* salt, $C_{27}H_{36}O_6N_4Cu$, m.p. 301°). H. W.



(*A*.)

Chlorophyll. CXVI. Purpurin 3, its meso-compound and derivatives. Synthesis of inactive mesopurpurin 3. H. Fischer and F. Gerner (*Annalen*, 1942, **553**, 67—82).—Attempts to oxidise mesophyllochlorin esters give negative results but free mesophyllochlorin is oxidised by finely-divided $KMnO_4$ in C_5H_5N to mesopurpurin 3, converted by CH_2N_2 into the Me_3 ester (**I**), m.p. 166°, which gives the typical reactions with NH_2OH and CN·CH_2·CO_2Et + NH_2Et and is identical with the substance obtained from *iso*chlorin e_4; 7 : 8-dihydroxymesophyllochlorin Me ester, m.p. 131°, is isolated as by-product. Synthetic mesophyllochlorin (from phyllohæmin) is similarly oxidised to optically inactive mesopurpurin 3, transformed into the Me_3 ester, m.p. 178°. (**I**) gives *salts*, $C_{33}H_{36}O_3N_4FeCl$, m.p. 182°, $[\alpha]^{20}_{\text{blue}}$ +4000° in $COMe_2$, and $C_{33}H_{36}O_3N_4Cu_3$, m.p. 173°, $[\alpha]_{\text{white}}$ ~+140° in $COMe_2$, which are remarkably stable, and $C_{33}H_{36}O_3N_4Zn$, m.p. 193, dextrorotatory in $COMe_2$, which is decomposed by 16% HCl. Purpurin 3 Me ester, (**II**), $MeNO_2$, and NH_2Et in C_5H_5N at 100° afford *γ-nitrovinylpyrrochlorin Me ester*, m.p. 197°, in ~80% yield. With CN·CH_2·CO_2Et and NH_2Et in C_5H_5N mesopurpurin 3 Me ester gives *Et mesopyrrochlorin-γ-α-cyanoacrylate Me ester*, m.p. 226°. Moist Ag_2O oxidises (**II**) in MeOH–dioxan containing C_5H_5N to 7 : 8-*dihydroxypurpurin* 3 *Me ester*, m.p. 196°, $[\alpha]_{\text{white}}$ +1500° in $COMe_2$, which gives a positive reaction with NH_2OH but appears indifferent to BzCl. With $KMnO_4$ in C_5H_5N (**II**) gives 2-*carboxy*-2-*devinylpurpurin* 3 Me_2 *ester*, m.p. 181°, $[\alpha]^{20}_{\text{blue}}$ +1250° in $COMe_2$. Unesterified purpurin 3 is transformed by MgEtBr followed by CH_2N_2 into *γ-γ′-hydroxypropylpyrrochlorin Me ester*, m.p. 211° $[\alpha]^{0}_{\text{green}}$ +1240° in $COMe_2$, which gives a positive reaction with BzCl and passes when heated into pyrrochlorin (**III**) and a *substance*, (?) $C_{38}H_{50}O_2N_4$, m.p. 189°, $[\alpha]^{20}_{\text{blue}}$ +1060° in $COMe_2$, which also reacts with BzCl, gives (**III**) when heated, and does not contain OMe. Attempts to prepare *γ-β′*-hydroxyethylpyrrochlorin Me ester are described. H. W.

Chlorophyll. CXVII. Partial synthesis of 6-formylmeso*iso*chlorin e_4. H. Fischer and F. Gerner (*Annalen*, 1942, **553**, 146—165).—The action of ClCO·NH_2 and $SnBr_4$ on the Cu derivative (**I**) of meso*iso*chlorin e_4 Me_2 ester in dry $CHCl_3$ gives *bromomeso-iso*chlorin e_4 Me_2 *ester*, decomp. ~130°, $[\alpha]^{20}_{\text{red}}$ −210°, $[\alpha]^{20}_{\text{blue}}$ +420° in $COMe_2$, which spectroscopically closely resembles mesomethylphæophorbide *a*. The Cu compound of mesophyllochlorin similarly yields *bromomesophyllochlorin Me ester*, decomp. ~120°, $[\alpha]^{20}_{\text{red}}$ ±0°, $[\alpha]^{20}_{\text{white}}$ +396°, $[\alpha]^{20}_{\text{green}}$ +993° in $COMe_2$, which passes when heated into mesophyllochlorin and phylloporphyrin. Under similar conditions the Cu compound (**II**) of mesopurpurin 3 is dehydrated to *γ*-formylpyrroporphyrin; if the CHO group is protected by oximation the product is *bromo-γ-formylpyrroporphyrin Me ester*, m.p. 224°, unchanged spectroscopically when heated with AcOH or KOH–MeOH. Gradual addition of $SnBr_4$ to (**I**) in CH_2Cl·OMe at 0° gives deoxophyllerythrin (**IV**), m.p. 268°, and a Cu complex (**III**), which, when shaken with HBr–AcOH, esterified with CH_2N_2, and extracted successively with 2% and 7% HCl affords *meso-iso-chlorin* e_4 6-*Me ester Me*$_2$ *ether*, m.p. 159°, $[\alpha]^{20}_{\text{blue}}$ −668° in $COMe_2$ (*Cu* derivative, m.p. 170°, $[\alpha]^{20}_{\text{blue}}$ −1260° in $COMe_2$), the spectrum of which is displaced towards the red in comparison with that of meso*iso*chlorin e_4 and is unchanged by AcOH or KOH–MeOH. The compound is stable towards cold conc. H_2SO_4 or $KMnO_4$–C_5H_5N but is converted by HI–AcOH at 70° into *iso*chloroporphyrin e_4. *Mesophyllochlorin* 6 *Me ether Me ester*, m.p. 168° (*Cu* derivative, m.p. 137°, $[\alpha]^{20}_{\text{blue}}$ −475° in $COMe_2$), is obtained analogously. Similarly (**II**) is transformed into a Cu derivative, converted by HBr–AcOH into *γ-formylpyrroporphyrin* 6 *Me ether Me ester*, m.p. 279°, and *γ*-formylpyrroporphyrin-6-carbinol which reacts with BzCl. Similarly successive treatments of (**III**) with HBr in AcOH and CH_2N_2 lead to *meso-iso-chlorin* e_4 6-*carbinol Me*$_2$ *ester*, m.p. 151°, $[\alpha]_{\text{white}}$ −505° in $COMe_2$, which is not changed spectroscopically by BzCl, and is converted by HI in AcOH at 70° into meso*iso*chlorin e_4 and *iso*chloroporphyrin e_4. It gives (**IV**) when heated with $(CH_2·CO)_2O$ at 220° or $AcCO_2H$ at 155°. In molten resorcinol it passes into deoxophæoporphyrin a_5, identified spectroscopically. It is oxidised by CrO_3 in AcOH to rhodoporphyrin-*γ*-carboxylic acid. It is oxidised by CrO_3 in C_5H_5N at 45° or, preferably, by $KMnO_4$ in AcOH to 6-*formylmeso-iso-chlorin* e_4 *Me*$_2$ *ester*, m.p. 159°, $[\alpha]^{20}_{\text{blue}}$ +1635° in $COMe_2$; NH_2OH or KOH in MeOH or PrOH induces the chlorin spectrum. 15% HCl causes rapid resinification. It is resistant to $KMnO_4$ or CrO_3 in C_5H_5N at 50° but is decomposed at higher temp. H. W.

Partial syntheses of devinyl- and 2-acetyl-2-devinylphyllochlorin. H. Fischer and F. Balat (*Annalen*, 1942, **553**, 166—186).—Optically inactive mesophyllochlorin Me ester is converted by $Fe(OAc)_2$ and NaCl in AcOH into the *salt*, $C_{33}H_{38}O_2N_4ClFe$, m.p. 237°, whereas the corresponding active salt has m.p. 246°; the *salt*, $C_{33}H_{38}O_2N_4Cu$, m.p. 150°, is obtained in the usual manner. The prep. of the active mesophyllochlorin Me ester (**I**) from chlorin e_6 is greatly improved by the substitution of boiling $C_{10}H_8$ for quinoline; vinylphylloporphyrin is obtained simultaneously in minor amount. The Fe^{II} complex salt of (**I**) is transformed by molten resorcinol at 175°, followed by successive treatments with $Fe(OAc)_2$ in AcOH and conc. HCl and then by extraction with 3% and then 8—10% HCl, esterification, and chromatography over Al_2O_3, into 2-*devinylphyllochlorin Me ester*, m.p. 156°, $[\alpha]_{690-720}$ −775° in $COMe_2$ (*salt*, $C_{31}H_{34}O_2N_4ClFe$, m.p. 209°, $[\alpha]^{20}_{690-720}$ -1000° in $COMe_2$). 2-Vinylphylloporphyrin Me ester is converted by $Fe(OAc)_2$ in AcOH containing NaCl into the *complex*, $C_{33}H_{34}O_2N_4ClFe$, m.p. 288°, which passes in resorcinol at 200° into a substance which after removal of Fe and esterification yields 2-*de-ethylphylloporphyrin Me ester*, m.p. 214° (*Fe* salt). The latter salt is treated successively with Na and boiling C_5H_{11}·OH under H_2, 15% HCl, $FeCl_3$ at 40°, and CH_2N_2, thus giving 2-*devinylphyllochlorin Me* ester (**III**), m.p. 147°, spectroscopically identical with the optically active material. (**III**) is converted by HBr–AcOH into 2-α-bromomesophyllochlorin, hydrolysed by 15% HCl and then esterified to 2-α-*hydroxymesophyllochlorin Me ester* (**IV**), m.p. 131°, $[\alpha]_{690-720}$ −657° in $COMe_2$. Analogously (**III**) is converted by HBr followed by boiling MeOH into 2-α-*methoxymesophyllochlorin Me ester*, amorphous, m.p. 130—140°, spectroscopically almost identical with (**IV**). Oxidation of (**IV**) by finely-powdered $KMnO_4$ in C_5H_5N leads to 2-*acetyl*-2-*devinylphyllochlorin Me ester* (**V**), m.p. 206° [*Zn* salt, m.p. 151°, hydrogenated (PtO_2 in MeOH) and then transformed by conc. HCl into (**IV**)]. BzCl and C_5H_5N convert (**IV**) into the *benzoate*. At 135°/0·1 mm., (**IV**) passes into phyllochlorin, m.p. 190°, $[\alpha]^{20}_{690-720}$ −832° in $COMe_2$, which gives a positive reaction with CHN_2·CO_2Et. In boiling C_5H_5N containing NH_2OH,HCl and anhyd. Na_2CO_3 (**V**) yields an *oxime*. The hæmin of (**III**) with $SnBr_4$ in Ac_2O with subsequent removal of Fe affords 2 : 6-*diacetyl*-2-*devinylphyllochlorin Me ester*, m.p. 199°, $[\alpha]^{0}_{690-720}$ −752° in $COMe_2$ (*dioxime*). (**III**) is converted by Br in $CHCl_3$–AcOH followed by CH_2N_2 into the *compound*, $C_{31}H_{33}O_2N_4Br_3$, m.p. 182°, the spectrum of which is greatly displaced towards the red in comparison with that of (**III**), and in which one Br appears to be labile. H. W.

Double invert soaps : symmetrical dimorpholinium salts. J. B. Niederl and E. J. Kenney (*J. Amer. Chem. Soc.*, 1944, **66**, 840—841).—By AlkBr in boiling 95% EtOH are prepared *methylenebis*-1-*morpholinium di*-n-*butyl*, m.p. 144° (decomp.), -n-*heptyl*, m.p. 141° (decomp.), -n-*octyl*, m.p. 143° (decomp.), -n-*tetradecyl*, m.p. 165° (decomp.), and -n-*hexadecyl dibromide*, m.p. 180° (decomp.), and *benzylidenebis*-1-*morpholinium di*-n-*butyl*, m.p. 174°, -n-*heptyl*, m.p. 153°, -n-*octyl*, m.p. 156°, -n-*tetradecyl*, m.p. 175°, and -n-*hexadecyl dibromide*, m.p. 178°. R. S. C.

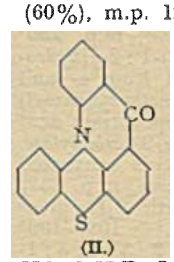
Two acid redox indicators of the oxazine series. Semiquinone theory. H. Eggers and H. Dieckmann (*Biochem. Z.*, 1942, **310**, 233—254).—*Na*. 3-*dimethylaminophenonaphthoxazine*-9 : 12-*disulphonate*, prepared by condensation of *R*-acid with *p*-NO·C_6H_4·NMe_2, or with *p*-NH_2·C_6H_4·NMe_2 followed by oxidation, and K_2 3-*dimethylaminophenonaphthoxazine*-7 : 9-*disulphonate* prepared by condensation of *G*-acid with *p*-NO·C_6H_4·NMe_2, are H_2O-sol. indicators, stable over a wide range of pH, and suitable for oxidation–reduction determinations. In aq. solution, a small amount of the dyes is present in the form of semiquinone radicals. The normal potentials for the dyes from *R*-acid and *G*-acid are +0·105 and +0·115 v., respectively. Light absorption by aq. solutions of the dyes does not obey Beer's law. Max. absorption with the *R*-acid and *G*-acid dyes are at 550 and 540 mμ., respectively. The dye derived from *R*-acid catalyses the oxidation of hæmoglobin to methæmoglobin by O_2.
J. N. A.

2-Amino-4-ω-carboxyalkylthiazoles. Their reaction with acetylsulphanilyl chloride. W. M. Ziegler (*J. Amer. Chem. Soc.*, 1944, **66**, 744—745).—Substitution by CO_2H·$[CH_2]_n$ hinders interaction of 2-aminothiazole with *p*-NHAc·C_6H_4·SO_2Cl (**I**), the effect being a max. at n = ~4 (cf. A., 1942, II, 153). CO_2Et·$[CH_2]_n$·CHAc·CO_2Et (n = 1, 2, 3, or 10) with Br–CS_2 at 0° (later room temp.) and then $CS(NH_2)_2$–H_2O at room temp. gives 2-*amino*-4-*αβ-dicarbethoxyethyl*-, m.p. 118—119°, -*αγ-dicarbethoxy*-n-*propyl*-, m.p. 87—88°, -*αδ-dicarbethoxy*-n-*butyl*-, m.p. 83—84°, and -*αλ-dicarbethoxy*-n-*undecyl-thiazole*, m.p. 79—80°, converted by boiling conc. aq. HCl–EtOH into γ-2-*amino*-4-*thiazylpropionic*, m.p. 213—214° (*hydrochloride*, m.p. 243—245°), δ-2-*amino*-4-*thiazyl*-n-*butyric*, m.p. (+H_2O) 99—101° or (anhyd.) 125—127° (*hydrochloride*, m.p. 207—209°), ε-2-*amino*-4-*thiazyl*-n-*valeric*, m.p. 202—203·5° (*hydrochloride*, m.p. 235—237°), and μ-2-*amino*-4-*thiazyl*-n-*dodecoic acid*, m.p. 105—107° (*hydrochloride*, m.p. 178—179·5°), respectively. With (**I**) in C_5H_5N at 100° and then boiling 2N-HCl, these give γ-2-*sulphanilamido*-4-*thiazylpropionic* (33%), m.p. 143—145° [*hydrochloride*, m.p. 277—279° (partial decomp.)], and δ-2-sulphanilamido-4-thiazyl-n-butyric acid (11%) [*hydrochloride*, m.p. 204—206° (partial decomp.)]; μ-2-N^4'-*acetylsulphanilamido*-4-*thiazyl*-n-*dodecoic acid* (40% yield), m.p. 98—100°, resists 2N-HCl and is destroyed by hot 2N-NaOH. The final products are ineffective against streptococci and pneumococci. M.p. are corr. R. S. C.

Preparation of *o*-aminobenzyl- and β-aminoethyl-thiazolium salts. H. T. Clarke (*J. Amer. Chem. Soc.*, 1944, **66**, 652).—*o*-NO_2·C_6H_4·CH_2Cl and 4-methylthiazole (**I**) in a little C_6H_6 at 95—100° give 3-*o*-*nitro*- (75%), decomp. 186·5—187°, reduced by Sn–SnCl₂–2N-HCl to 3-*o*-amino-benzyl-4-methylthiazolium chloride (*hydrochloride*, decomp. 204—212°). *o*-$C_6H_4(CO)_2N$·$[CH_2]_2$·Br and (**I**) at 95—100° give 4-*methyl*-3-*β-phthalimidoethyl*-, m.p. 238° (slight decomp.), and thence (boiling 48% HBr) 4-methyl-3-β-aminoethyl-thiazolium bromide [*hydrobromide*, m.p. 222·5—223·5° (decomp.)]. R. S. C.

Sulphonamides in the benziminazole, benzthiazole, and benztriazole series. C. F. H. Allen, A. Bell, and C. V. Wilson (*J. Amer. Chem. Soc.*, 1944, **66**, 835—837).—Methods of preparing SO_2R derivatives of these heterocyclic systems are developed.
o-NO_2·C_6H_4·NH·CO·CO_2Et and $ClSO_3H$ at 100° give 3 : 4 : 1-NO_2·$C_6H_3(NH_2)$·SO_2Cl, m.p. 152—153° [obtained in only 3—4% yield from *o*-NO_2·C_6H_4·NH_2 by $ClSO_3H$; derived amide (**I**), m.p. 206—207°], which with NH_2R and KOAc or NaOAc in AcOH gives 3-*nitro*-4-*aminobenzenesulphon*-p-*acetamidoanilide*, m.p. 265—266°, and -*o*-*hydroxyanilide* (**II**), m.p. 205—206°. 3 : 4 : 1-NO_2·C_6H_3Cl·SO_2Cl (**III**) gives similarly 4-*chloro*-3-*nitrobenzenesulphon*-p-*chloro*- (**IV**), m.p. 120—121° -p-*acetamido*-, m.p. 188—190°, -*o*-*hydroxy*-, m.p. 143—145°, and -2'-*hydroxy*-4'-*methyl*-, m.p. 155—156°, -*anilide*. H_2–Raney Ni or $Na_2S_2O_4$ reduces (**I**) to 3 : 4-*diaminobenzenesulphonamide*, m.p. 174—175°, which with HNO_2 gives *benztriazole*-5-*sulphonamide*, m.p. 236—237°, or with HCO_2H or AcOH gives *benziminazole*-, m.p. 213—214°, and 2-*methylbenziminazole*-5-*sulphonamide*, m.p. 221°, respectively. With OH·$[CH_2]_2$·NH_2 (**V**) in boiling C_5H_5, (**III**) gives 4-*chloro*-3-*nitro*-, m.p. 125°, but with an excess of (**V**) gives 3-*nitro*-4-*β-hydroxyethylamino-benzenesulphon*-*β-hydroxyethylamide*, m.p. 158°. 3 : 4 : 1-NO_2·C_6H_3Cl·SO_2·NHR with 1 : 1 85% N_2H_4,H_2O–EtOH at the b.p. gives 1-*hydroxybenztriazole*-5-*sulphon*-*amide*, m.p. 222° (decomp.), -*o*-*hydroxyanilide*, m.p. 228° (decomp.), and -*β-hydroxyethylamide*, m.p. 168° (decomp.). H_2–Raney Ni in EtOH at 90°/40 lb. reduces (**II**) to the diamine, which with CS_2 and 40% NaOH at the b.p. yields 2-*thiolbenziminazole*-5-*sulphon*-*o*-*hydroxyanilide*, m.p. 265° (decomp.). 2-*Thiolbenziminazole*-5-*sulphon*-p-*acetamidoanilide* (similarly prepared) in conc. HCl–EtOH at the b.p. gives the p-*aminoanilide*, m.p. 240—242° (decomp.). Hot aq. Na_2S–S converts (**IV**) into 2-*thiolbenzthiazole*-5-*sulphon*-p-*chloroanilide*, m.p. 208—210° (decomp.). 2-*Thiolbenzthiazole*-5-*sulphon*-p-*acetamido*-, m.p. 284—285° (decomp.), -*o*-*hydroxy*-, m.p. 246—248° (decomp.), and -2'-*hydroxy*-4'-*methyl*-*anilide*, m.p. 218—220° (decomp.), are similarly prepared. R. S. C.

Metalation of phenthiazine. H. Gilman, D. A. Shirley, and P. R. Van Ess (*J. Amer. Chem. Soc.*, 1944, **66**, 625—627).—Adding LiPh–Et_2O–N_2 to phenthiazine (**I**), keeping for 35 hr., then pouring the mixture onto Et_2O–solid CO_2, and finally hydrolysing with H_2O gives *phenthiazine*-1-*carboxylic acid* (52%), m.p. 264—264·5°, the Me ester, m.p. 113—113·5°, of which with PhI, K_2CO_3, and Cu-bronze at the b.p. yields *Me* 10-*phenylphenthiazine*-1-*carboxylate* (60%), m.p. 123·5—124·5°. Structures are proved by cyclisation of the derived acid by PCl_5–xylene at room temp. and then $SnCl_4$–xylene at 0° to 9-*quino*[3, 2, 1-kl]-*phenthiazone* (**II**), (85%), m.p. 218—219°. *o*-C_6H_4I·CO_2Me, (**I**), K_2CO_3, and Cu-bronze in xylene–$PhNO_2$ give 10-*o*-*carbomethoxyphenylphenthiazine* (42%), m.p. 143—144°; ring-closure of the derived (15% aq. KOH) *acid*, m.p. 214—215°, as above yields 60% of (**II**), proving the structure of the latter. Conversion of 2-*carbethoxydiphenylamine*, b.p. 184—187°/6 mm., by S etc. into phenthiazine and coupling of (*o*-NH_2·C_6H_4·S)$_2$ with 3 : 2 : 1-NO_2·C_6H_3Br·CO_2H–NaOAc–EtOAc at the b.p. or with *o*-C_6H_4Cl·CO_2K–NaOAc–Cu-bronze–C_5H_{11}·OH at the b.p. could not be achieved. R. S. C.



(II.)

Hemicyanine dyes.—See B., 1944, II, 244.

VII.—ALKALOIDS.

Total synthesis of quinine. R. B. Woodward and W. E. Doering (*J. Amer. Chem. Soc.*, 1944, **66**, 849).—The following synthesis is briefly recorded. 7-Hydroxy*iso*quinoline → 7-*hydroxy*-8-*piperidinomethyl*-, m.p. 81·5—82·5°, → 7-*hydroxy*-8-*methyl*-, m.p. 232—233·5°, → (H_2–PtO_2) 7-*hydroxy*-8-*methyl*-1 : 2 : 3 : 4-*tetrahydro*-, m.p. 246—250°, → 7-*hydroxy*-1-*acetyl*-8-*methyl*-1 : 2 : 3 : 4-*tetrahydro*-, m.p. 191—198° → (H_2–Raney Ni) mixed 7-*hydroxy*-1-*acetyl*-8-*methyldecahydro*- (cis-*compound*, m.p. 126—128°; *cis* refers to ring-junctions) → mixed cis-7-*keto*-1-*acetyl*-8-*methyldecahydro*-isoquinoline, +H_2O, m.p. 80·5—82·5° → (OEt·NO–NaOEt) 10-*oximino*-1-*acetylhomomeroquinene Et* ester, dimorphic, m.p. 96—98° (labile) and 108·5—109·5°, → the 10-NH_2-compound (*H*$_2$-derivative, +$2H_2O$, m.p. 186·5—188°) (MeI–K_2CO_3) quaternary *iodide* → (alkali) dl-*homomeroquinene*, m.p. 219—220° (decomp.) [isolated by way of the *carbamide* derivative, m.p. 165·2—165·8° (decomp.)] → *N*-benzoylhomomeroquinene Et ester. By condensation with Et quininate etc. by Rabe's and Prelog's methods this yields *dl*-quinotoxine, whence *d*-quinotoxine, an oil, $[\alpha]_D$ +43°, is obtained by means of its dibenzoyl-*D*-tartrate, m.p. 185·5—186°. With earlier work this constitutes a total synthesis of quinine. R. S. C.

Colchicine and related compounds. III. J. W. Cook, W. Graham, and (in part) A. Cohen, R. W. Lapsley, and C. A. Lawrence. **IV. Synthesis of 2 : 3 : 4 : 5-, 2 : 3 : 4 : 6-, and 2 : 3 : 4 : 7-tetramethoxy-9-methylphenanthrenes.** G. L. Buchanan, J. W. Cook, and J. D. London (*J.C.S.*, 1944, 322—325, 325—329).—III. 3 : 4 : 5-*Trimethoxy-benzanilide*, m.p. 136—137°, prepared from the corresponding benzoyl chloride and NH_2Ph, with PCl_5 gives the chloro-imine, reduced ($SnCl_2$–HCl) to the -benzaldehyde, the *diacetate*, m.p. 112—113°, of which yields no cryst. nitration product. α-Cyano-α-*p*-anisyl-β-(3 : 4 : 5-trimethoxyphenyl)ethylene is brominated to the 2-*Br*-compound (**I**), m.p. 141—142·5°, hydrolysed (6N-NaOH) to a mixture of α-p-*anisyl*-β-(2-*bromo*-3 : 4 : 5-*trimethoxyphenyl*)*acrylamide*, m.p. 179—181°, and a gum oxidised ($KMnO_4$) to 3 : 4 : 5 : 2 : 1-$(OMe)_3C_6HBr$·CO_2H; (**I**) could not be cyclised. 2 : 3 : 4 : 5 : 1-NO_2·$C_6H(OMe)_3$·CHO and *p*-OMe·C_6H_4·CH_2·CN afford α-*cyano*-α-p-*anisyl*-β-(2-*nitrotrimethoxyphenyl*)*ethylene*, m.p. 164·5—165·5°. 3 : 4 : 5 : 1-$(OMe)_3C_6H_2$·CHO and *p*-OH·C_6H_4·CH_2·CN give α-*cyano*-α-p-*hydroxyphenyl*-β-(3 : 4 : 5-*trimethoxyphenyl*)*ethylene*, m.p. 169·5—170·5°, which is reduced (Na–EtOH) to α-p-*hydroxyphenyl*-β-(3 : 4 : 5-*trimethoxyphenyl*)*acrylamide*, m.p. 211°. 3 : 4 : 5 : 1-$(OMe)_3C_6H_2$·CH_2·OH (3 : 5-*dinitrobenzoate*, m.p. 147—148°), obtained by reduction of the aldehyde, with $SOCl_2$ and $NPhMe_2$ gives the *chloride* (**II**), m.p. 60—61°. 3 : 4 : 5 : 1-$(OMe)_3C_6H_2$·CH_2·OH may also be prepared by methylation (MeI–NaOEt) of the syringic alcohol, m.p. 131—132°, obtained from 1 : 3-dimethylpyrogallol and aq. CH_2O–NaOH; if the methylation is carried out with C_6H_4Me·SO_3Me, the product is 1 : 2 : 3 : 5 : 6 : 7-*hexamethoxy*-9 : 10-*dihydroanthracene*, m.p. 201°. 4-Methoxy*cyclo*hexanone is brominated to the 2-Br-compound (**III**), the identity of which is shown by its conversion by $CS(NH_2)_2$ into 2-*amino*-6-*methoxy*-4 : 5 : 6 : 7-*tetrahydrobenzthiazole*, m.p. 141·5—144°. $CH_2(CO_2Et)_2$ and Na with (**II**) give *Et* 3 : 4 : 5-*trimethoxybenzylmalonate*, m.p. 67—71° (hydrolysed and decarboxylated to β-3 : 4 : 5-*trimethoxyphenylpropionic acid*, m.p. 100—102°), the Na compound of which with (**III**) forms, after hydrolysis, not the required product but a mixture containing 3 : 4 : 5-*trimethoxybenzylmalonic acid*, m.p. 115—116°. 2 : 4 : 1-$(NO_2)_2C_6H_3$·CH_2·CO_2Me with N_2H_4 affords

2 : 4-*dinitrophenylacethydrazide*, m.p. 135·5—137°. A series of experiments with 3 : 4 : 5 : 1-$(OMe)_3C_6H_2$·CH_2·CO·NH_2 has failed to give the required methoxylated phenanthrenes. P_2O_5 with *N*-acetylcolchinol Me ether gives the same product (**IV**) as that obtained by Hofmann degradation of colchinol Me ether (cf. Windaus, A., 1924, i, 1089). Colchicine and CN·CH_2·CO·NH_2 yield a *product*, decomp. 205°, which is probably a quinoline or *iso*quinoline derivative.

IV. 3 : 4 : 5 : 1-$(OMe)_3C_6H_2$·COCl with anhyd. HCN in quinoline gives 1-(3′ : 4′ : 5′-*trimethoxybenzoyl*)-1 : 2-*dihydroquinaldinonitrile*, m.p. 176—177°, hydrolysed (H_2SO_4) to 3 : 4 : 5 : 1-$(OMe)_3C_6H_2$·CHO, also obtained through 3 : 4 : 5-*trimethoxybenzhydrazide* (+MeOH), m.p. 128—129°, and the *benzenesulphonyl* derivative, m.p. 250° (decomp.). 1-(o-, m.p. 173°, and 1-(m-*nitrobenzoyl*)-1 : 2-*dihydroquinaldinonitrile*, m.p. 171°, are similarly prepared from *o*- and *m*-NO_2·C_6H_4·CHO, and the 1-(2′-*nitro*-3′ : 4′ : o -*trimethoxybenzoyl*) compound, m.p. 168°, is also prepared from the appropriate acid chloride. *Me* 2 : 3 : 4 : 6-*tetramethoxyphenanthrene*-9-*carboxylate*, m.p. 96—97°, prepared from the acid with CH_2N_2, is converted through the hydrazide and *benzenesulphonyl* derivative, m.p. 237° (decomp.), into the -9-*aldehyde*, m.p. 119°, which with N_2H_4 gives 2 : 3 : 4 : 6-*tetramethoxy*-9-*methylphenanthrene*, m.p. 108—109° (*picrate*, m.p. 115°). *m*-OMe·C_6H_4·CH_2·CO_2Na and 2 : 3 : 4 : 5 : 1-NO_2·$C_6H(OMe)_3$·CHO with Ac_2O, followed by acidification, yield a mixture of cis-, m.p. 139—140° (main product), and trans-2-*nitro*-3 : 4 : 5-*trimethoxy*-α-m-*methoxyphenylcinnamic acids*, m.p. 181°, reduced (aq. NH_3–$FeSO_4$) respectively to the 2-*NH*$_2$-*acid*, m.p. 162°, and 6 : 7 : 8-*trimethoxy*-3-(m-*methoxyphenyl*)*carbostyril*, m.p. 185—186°. The diazotised NH_2-acid is decomposed in Na_2CO_3 solution to a mixture of 2 : 3 : 4 : 7-, m.p. 236°, and 2 : 3 : 4 : 5-*tetramethoxyphenanthrene*-9-*carboxylic acids*, m.p. 162—163° and subsequently 185°. A series of experiments leads to 2 : 3 : 4 : 7-*tetramethoxy*-9-*methylphenanthrene*, m.p. 116—117° (*picrate*, m.p. 150°), through the *Me* ester, m.p. 103°, *hydrazide*, m.p. 199°, *benzenesulphonhydrazide*, m.p. 250°, and the *aldehyde*, m.p. 134—135°. 2 : 3 : 4 : 5-*Tetramethoxy*-9-*methylphenanthrene*, m.p. 102° (*picrate*, m.p. 135°), is similarly obtained through the *hydrazide*, m.p. 182°, *benzenesulphonhydrazide*, m.p. 232°, and the *aldehyde*, m.p. 92°. None of the three -9-methylphenanthrenes is identical with (**IV**), to which the structure 2 : 3 : 4 : 6(or 7)-tetramethoxy-9-methylphenanthrene had been assigned. F. R. S.

Ultra-violet absorption spectra od solutions of yohimbine, corynanthine, corynantheine, and some of their derivatives.—See A., 1944, I, 191.

VIII.—ORGANO-METALLIC COMPOUNDS.

Action of cæsium on ethylene. L. Hackspill and R. Rohmer (*Compt. rend.*, 1943, **217**, 152—153).—Cs and C_2H_4 slowly form a solid *substance*, $C_2H_4Cs_2$, hydrolysed quantitatively to CsOH and C_2H_6. F. R. S.

Long-chained organo-metallic compounds. R. N. Meals (*J. Org. Chem.*, 1944, **9**, 211—218; cf. A., 1944, II, 66).—A series of long-chained organo-metallic compounds of Li, Na, K, Ca, Hg, As, Sn, and Pb has been prepared. The NaR, KR, and CaRI types examined are insol. in hydrocarbons including the kerosene fractions. Incidental to the prep. of these MR compounds there are formed R(−H), R·H, and R·R hydrocarbons as a consequence of disproportionation and coupling reactions. The prep. of $NaC_{12}H_{25}$-*n* in poor yield in Et_2O is of interest because of the ready cleavage of Et_2O by the simpler NaAlk compounds. Compounds LiR can be prepared in several solvents, the most suitable appearing to be light petroleum, b.p. 60—70°. Substances RCl are most suitable for the prep. of LiR types. 1 : 2 : 3-$C_6H_3(OMe)_3$ is metallated by $LiC_{12}H_{25}$-*n* in an *ortho*-position to give 2 : 3 : 4 : 1-$(OMe)_3C_6H_2$·CO_2H on subsequent carbonation. The long-chained organo-mercury halides are not particularly suitable as derivatives for rigid differentiation of contiguous, even-membered types. Thus $HgC_{16}H_{33}Cl$, $HgC_{18}H_{37}Cl$, and an equinol. mixture of them have m.p. 114—115°, 115—116°, and 113° respectively. Compounds $SnAlk_3Cl$ and $PbAlk_3Cl$ show greater differences in m.p. between homologues than do the Hg alkyl chlorides, but they are only of limited applicability as derivatives for differentiation of contiguous, even-membered homologues because of the small m.p. depressions of mixtures. $Sn(C_{16}H_{33})_4$ and $Pb(C_{16}H_{33})_4$ have m.p. 41·5—42·5° and 42°, respectively, and a mixture of equal parts of them melts at 42°. The following are reported in addition to those listed previously (*loc. cit.*): *Hg dodecyl acetate*, m.p. 64—65°; (*Hg docedyl*)$_2$ *sulphate*, m.p. 160—161°; (*Hg dodecyl*)$_3$ *phosphate*, m.p. 84—86°; *Hg octadecyl cyanide*, m.p. 98·5—99°; *Pb tri*-n-*dodecyl nitrate*, m.p. 44—45°, and *acetate*, m.p. 59°. The m.p. for the compounds $Hg(C_{12}H_{25})_2$, $Hg(C_{14}H_{29})_2$, $Hg(C_{16}H_{33})_2$, and $Hg(C_{18}H_{37})_2$ show a regular variation with chain length expressible by the relationship $M - 32 \pm 13\sqrt{(n-11)}$, where M is the m.p. and n the no. of C of the alkyl group. H. W.

Phenolic mercurials. J. B. Niederl and A. J. Shukis (*J. Amer. Chem. Soc.*, 1944, **66**, 844).—The appropriate phenol with the requisite amount of $Hg(OAc)_2$ in 1 : 10 : 10 AcOH–EtOH–H_2O at the b.p. give 2-*acetoxymercuri*-, m.p. 158° (corresponding *HgCl* compound, m.p. 161°), 2 : 6-*diacetoxymercuri*-, m.p. 181° [corresponding $(HgCl)_2$ compound, m.p. 238° (decomp.)], 3-*hydroxy*-2 : 6-*diacetoxymercuri*-, m.p. 183° (decomp.), 2-*acetoxymercuri*-6-*methyl*-, m.p. 149°, -4-*aαγγ-tetramethyl*-n-*butylphenol*, 1 : 1-*di*-4′-*hydroxy*-2′-*acetoxymercuri*-6′-*methyl*-, m.p. 200° (decomp.) [corresponding $(HgCl)_2$ compound, m.p. 225° (decomp.)], and 1 : 1-*di*-4′-*hydroxy*-2′ : 6′-*diacetoxymercuri*-, m.p. 210° (decomp.) [corresponding $(HgCl)_4$ compound, m.p. 222° (decomp.)], -*phenylcyclohexane*, and *ββεε-tetra*-4′-*hydroxy*-2′ : 6′-*diacetoxymercuriphenyl*-n-*hexane*, m.p. 308° (decomp.) [corresponding $(HgCl)_8$ compound, m.p. 247° (decomp.)]. R. S. C.

Preparation of aromatic mercury salts of organic acids.—See B., 1944, III, 169.

Organomagnesium compounds. II. Reaction of Grignard reagents with carbonyl compounds. A. N. Nesmejanov and V. A. Sazonova (*Bull. Acad. Sci. U.R.S.S., Cl. Sci. Chim.*, 1941, 499—517).—Using filtered and titrated Grignard reagents in an atm. of N_2, it is shown that the same compound CRR′R″·O·MgX,Et_2O is produced in all three reactions: (i) COR′R″ + MgRX,Et_2O, (ii) CORR′ + MgR″X,Et_2O, and (iii) CRR′R″·OH + MgEtX,Et_2O. The reaction product is thus a true alcoholate, as originally formulated by Grignard (A., 1902, i, 142) and contrary to the later views of Hess *et al.* (A., 1921, i, 777; 1924, i, 859), Meisenheimer *et al.* (A., 1921, i, 654; 1925, i, 527; 1926, 68), and Pfeiffer and Blank (A., 1939, II, 360), who postulate the formation of complexes which may or may not undergo internal rearrangement. The work of these authors is criticised in detail.

CHPhEt·OH (**I**) and MgEtBr in Et_2O afford CHPhEt·O·MgBr,Et_2O (**II**), biaxial prisms with negative optical sign and $r > v$[1], stable in dry air and converted by EtOAc into the acetate of (**I**) and by *p*-NO_2·C_6H_4·COCl into the *p*-nitrobenzoate of (**I**). The Et_2O in (**II**) can be removed by heating and partly replaced by PhCHO, the exchange being reversible. (**II**) with dil. H_2SO_4 affords C_2H_6. (**II**) is also formed from PhCHO and MgEtBr, the identity of the product being confirmed by the cryst. form, solubility in Et_2O, action of EtOAc and *p*-NO_2·C_6H_4·COCl, and formation of C_2H_6 from (**I**) by decomp. with aq. NH_4Cl; no C_2H_4 is produced by heating (**II**) in C_6H_6. EtCHO and MgPhBr in Et_2O also give (**II**), identified as before. CPhMeEt·OH and MgEtBr in Et_2O afford CPhMeEt·O·MgBr,Et_2O (**III**), biaxial prisms with negative optical sign and $v > r$. It is converted by EtOAc into an ester, decomp. on distillation, and does not react with *p*-NO_2·C_6H_4·COCl. The Et_2O can be removed on heating with partial decomp. (**III**) is also formed from MgEtBr and COPhMe in Et_2O, identified as above by optical properties and solubility in Et_2O. MgEtBr and $COPh_2$ in cold Et_2O afford CPh_2Et·O·MgBr,Et_2O (**IV**), giving CPh_2Et·OH with aq. NH_4Cl and no $COPh_2$. If the reaction mixture was boiled for 5 hr. some $CPh_2{:}CH_2$ was also isolated. $MgBu^{\beta}Br$ and $COPh_2$ in Et_2O afford $CHPh_2$·O·MgBr,Et_2O (**V**), biaxial pyramids with positive optical sign and $r > v$, giving $CHPh_2$·OAc with EtOAc; (**V**) is also formed from $CHPh_2$·OH and MgEtBr in Et_2O. MgPhBr and fenchone (**VI**) in Et_2O afford a cryst. *compound*, which has not the expected formula $C_{10}H_{16}O$,MgPhBr,Et_2O (cf. Leroide, A., 1909, i, 596) and contains no MgPhBr, as it does not give Gilman's reaction or form C_6H_6 with H_2O, although it regenerates (**VI**). *p*-NH_2·C_6H_4·COPh and MgEtBr in Et_2O give C_2H_6 corresponding to 1 H of the NH_2 and therefore form the compound COPh·C_6H_4·NH·MgBr. G. A. R. K.

Trimethylsilane and silicon trimethyl chloride. A. G. Taylor and B. V. de G. Walden (*J. Amer. Chem. Soc.*, 1944, **66**, 842—843).—$SiHCl_3$ [prep. from ferrosilicon (95—97% Si)] and MgMeBr in Et_2O give $SiHMe_3$, b.p. 9—11°, which with Cl_2 at −20° yields $SiMe_2Cl$ (75%), f.p. ~−40°, b.p. 57—59·4°/747 mm. [v.p. given for 28·9° (308 mm.) to 56·1° (720 mm.)]. R. S. C.

IX.—PROTEINS.

Precipitation of proteins by synthetic detergents. F. W. Putnam and H. Neurath (*J. Amer. Chem. Soc.*, 1944, **66**, 692—697).—Pptn. of six proteins by *n*-$C_{12}H_{25}$·$NaSO_4$ (**I**) occurs at pH > the isoelectric point; for human carboxyhæmoglobin (isoelectric point 7·1) this pH is 6·4. At > this pH no pptn. occurs and ppts. formed at lower pH are redissolved by adjusting the pH to > the isoelectric point. The following are established for horse serum-albumin. The lower is the pH, the faster is the rate of coagulation, but the wt. of ppt. is const. The wt. of ppt. ∝ concns. of protein and (**I**), and also increases with temp. The pH of protein solutions, previously adjusted to the isoelectric point, is gradually increased from 4·85 to ~6·4 by adding increasing amounts of (**I**). Treating the ppt. with $Ba^{\cdot\cdot}$ yields (*n*-$C_{12}H_{25}$·$SO_4)_2Ba$ and a solution of recovered protein, which is shown by electrophoresis, diffusion, and η to be homogeneous but partly denatured. Possible applications of the pptn. are mentioned. R. S. C.

Diplococcein, antibacterial protein from milk streptococci.—See A., 1944, III, 615.

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A II—Organic Chemistry

NOVEMBER, 1944.

I.—ALIPHATIC.

Rearrangement of alkyl halides.—See A., 1944, I, 252.

Preparation of *aaa*-trichloropropane.—See B., 1944, II, 269.

Oxidations [of dienes] by hydrogen peroxide in presence of selenious anhydride. P. Seguin (*Compt. rend.*, 1943, **216**, 667—668).—SeO_2 is more convenient than OsO_4 or V_2O_5 for oxidations by means of H_2O_2. To limit the oxidation to one of two double linkings, the best solvent is $Bu^{\gamma}OH$. Second to this is $COMe_2$, although this is itself partly oxidised. The reaction should be carried out with conc. solutions, as otherwise it is liable to be lengthy. Experiments on *cyclo*hexene (**I**) show that 4 g. of SeO_2 are required per g.-mol. of the substance being oxidised. The oxidation is complete in about a week, but may be regarded as practically complete after 48 hr. In the oxidation of (**I**) a 45% yield of *trans-cyclo*hexanediol was obtained with no trace of the *cis*-compound, whereas when OsO_4 is used, a mixture of *cis*- and *trans*-compound is obtained. In the oxidation of dienes, 2 OH add on across 1 : 2 rather than 1 : 4. *cyclo*Pentene-1 : 2-diol was obtained from *cyclo*pentadiene. Piperylene gave a mixture of CHMe:CH·CH(OH)·CH_2·OH and a little CH_2:CH·CH(OH)·CHMe·OH. $(CHPh:CH)_2$ was very resistant to oxidation. A. J. M.

Solubilities of high mol. wt. normal aliphatic primary alcohols.—See A., 1944, I, 221.

Manufacture of unsaturated alcohols.—See B., 1944, II, 246.

Properties of Δ^{δ}-penten-α-ol. Preparation of divinylmethane. R. Paul and H. Normant (*Compt. rend.*, 1943, **216**, 689—691).—2-Methyltetrahydrofuran (**I**) is obtained from CH_2:CH·$[CH_2]_3$·OH (**II**) by distilling with conc. H_2SO_4 (88% yield) or, less well, by $NaHSO_4$–pumice at 170°. Al_2O_3 at 390° converts (**I**) into CHMe:CH·CH:CH_2 (15%) and (**II**) (11%). Passing CH_2:CH·$[CH_2]_3$·OAc over glass wool at 560° gives $CH_2(CH:CH_2)_2$ (60%), b.p. 26—27° (tetrabromide, m.p. 85·5—86°). R. S. C.

Manufacture of acylated secondary alcohols.—See B., 1944, II, 246.

Manufacture of ethers from olefines.—See B., 1944, II, 271.

Glyceryl α-*n*-dodecyl ether. O. Grummitt and R. F. Hall (*J. Amer. Chem. Soc.*, 1944, **66**, 1229—1230).—*n*-$C_{12}H_{25}$·OH (2 mols.), epichlorohydrin (1 mol.), and a little anhyd. $FeCl_3$ at 160° give $CH_2Cl·CH(OH)·CH_2·O·C_{12}H_{25}$-*n* (39%; less in absence of $FeCl_3$ or with other proportions of reagents), b.p. 157°/1 mm., converted by NaOH in boiling Bu^{α}_2O into *βγ-epoxy-n-propyl* n-*dodecyl ether* b.p. 132—135°/1—2 mm., whence 5% H_2SO_4 at 160° (not boiling dil. HCl) (apparatus: C, 1944, Part 4) gives *glyceryl* α-n-*dodecyl ether* (78%), m.p. ~20° [oxidised quantitatively, but slowly, by $Pb(OAc)_4$ in AcOH]. R. S. C.

Preparation and catalytic reduction of γ-nitro-β-butyl *p*-nitrobenzoate. J. R. Reasenberg and G. B. L. Smith (*J. Amer. Chem. Soc.*, 1944, **66**, 991—994).—MeCHO and $EtNO_2$ with NaOH–EtOH–H_2O (a little) at room temp. give NO_2·[CHMe]$_2$·OH (**I**), b.p. 90°/11 mm., reduced (H_2–Raney Ni; EtOH; 3—4 atm.) to NH_2·[CHMe]$_2$·OH (**II**), b.p. 159° [H oxalate, m.p. 164° (decomp.); oxalate, m.p. 206° (decomp.)], there being no evidence of formation of stereoisomerides (cf. Vanderbilt *et al.*, A., 1940, II, 62). With *p*-$O_2N·C_6H_4$·COCl in C_5H_5N at <25°, (**I**) gives a mixture, m.p. 85—90°, of stereoisomerides, whence repeated crystallisations or, better, two treatments with 0·1 mol. of NaOH in hot aq. EtOH give a pure *γ-nitro-β-*p-*nitrobenzoyloxy*-n-*butane* (**III**), m.p. 107—108°; isomeride is more readily hydrolysed or converted into NO_2·CMe.CHMe and is thus lost. With 3 H_2 in presence of Raney Ni and a $PtCl_4$ in dioxan or in presence of PtO_2 as catalyst, (III) gives *α-nitro-β-*p-*aminobenzoyloxy*-n-*butane* (**IV**), m.p. 101—102° [*hydrochloride* (**V**), m.p. 182—183° (decomp.; rapid heating); trate m.p. 167—169° (decomp.; rapid heating); *Ac* derivative, p. With PtO_2 (not Ni) in EtOH, (**V**) is hydrogenated to *γ-nitro-β-4-amino*cyclo*hexanecarboxyloxy*-n-*butane hydrochloride*, ecomp. 177° (slow heating) or 184° (rapid heating) (derived *platini-* PtO_2 ı OH, (**I**) gives by reduction and spontaneous rearrangent *β-*p-*aminobenzamido-γ-hydroxy*-n-*butane* (**VI**), m.p. 145—146° (hydrochloride; acetate, m.p. 145—146°). (**II**) yields *p*-$NO_2·C_6H_4·CO·NH·[CHMe]_2·OH$, m.p. 158°, whence (**VI**) is obtained by H_2–Raney Ni in EtOH. (**VI**) is also obtained from (**IV**) by H_2–Raney Ni. All reductions to (**VI**) give also small amounts of a *substance*, $C_{15}H_{24}N_2O_2$, an anæsthetic oil (*Ac*$_2$ derivative, m.p. 151°; *picrate*, m.p. 171·5—172°). R. S. C.

Alkyl sulphites. *cyclo*Hexyl sulphite. L. P. Kyrides (*J. Amer. Chem. Soc.*, 1944, **66**, 1006—1007).—Adding $SOCl_2$ to *cyclo*hexanol at 25°/vac., falling to 5°/vac., and then slowly raising the temp. to 55° gives 93·5% of di*cyclo*hexyl sulphite, b.p. 165°/4 mm., which is stable although it smells of SO_2 and *cyclo*hexene (cf. Voss *et al.*, A., 1935, 1492; Carré *et al.*, *ibid.*, 480). Me$_2$, b.p. 124—127°, Et$_2$ b.p. 154—157°, Pr$^{\beta}_2$, b.p. 73—74°/25 mm., Bu$^{\alpha}_2$, b.p. 124—126°/29 mm., and di-β-octyl sulphite, b.p. 147—149°/0—6 mm., are similarly prepared in excellent yields. R. S. C.

Unsaturated synthetic glycerides. VII. Preparation and properties of synthetic α-monoglycerides and simple triglycerides of linoleic and linolenic acids. B. F. Daubert and A. R. Baldwin (*J. Amer. Chem. Soc.*, 1944, **66**, 997—1000; cf. A., 1944, II, 287).—*iso*Propylideneglycerol with linolenyl or linoleyl chloride (1 mol.) in quinoline–$CHCl_3$ at room temp. and then aq. HCl–Et_2O at ~0° gives *α-monolinolenin*, *forms*, m.p. —13·5° and 15·7° (*hexabromide*, m.p. 172°), and α-monolinolein, *forms*, m.p. —22·8° and 12·3° (hexabromide, m.p. 101·5°), respectively. Trilinolenin, *forms*, m.p. —44·6° and —24·2°, and trilinolein, *forms*, m.p. —45·6° and —12·9° (cf. Wheeler *et al.*, A., 1940, II, 116), are prepared at 100°. R. S. C.

Preparation of cyanomethyl chloroformate. See B., 1944, II, 246.

***tert.*-Butyl trichloroacetate.** W. E. Scovill, R. E. Burk, and H. P. Lankelma (*J. Amer. Chem. Soc.*, 1944, **66**, 1039).—*Bu$^{\gamma}$ trichloroacetate*, m.p. 25·5°, b.p. 37°/1 mm., is obtained (95%) from CCl_3·COCl and $Bu^{\gamma}OH$ in C_5H_5N or (80%) from $CCl_3·CO_2H$ and CH_2:CMe_2. R. S. C.

Preparation and properties of *n*-alkyl acrylates. C. E. Rehberg and C. H. Fisher (*J. Amer. Chem. Soc.*, 1944, **66**, 1203—1207).—Good yields of Et, b.p. 43°/103 mm., Pr$^{\alpha}$, b.p. 44°/40 mm., Bu$^{\alpha}$, b.p. 35°/8 mm., *n*-amyl, b.p. 48°/7 mm., *n*-hexyl, b.p. 40°/1·1 mm., *n*-heptyl, b.p. 57°/1 mm., *n*-octyl (**I**), b.p. 57°/0·05 mm., *n*-nonyl, b.p. 76°/0·2 mm., *n*-decyl, b.p. 120°/5 mm., *n*-dodecyl, m.p. ~4°, b.p. 120°/0·8 mm., *n*-tetradecyl, m.p. ~14°, b.p. 138°/4 mm., and *n*-hexadecyl acrylate (**II**), m.p. ~24°, b.p. 148°/0·04 mm., are obtained by heating CH_2:CH·CO$_2$Me (**III**), b.p. 80°, ROH, a little H_2SO_4 [or, less well, *p*-C_6H_4Me·SO_3H, Al(OBu$^{\gamma}$)$_3$, or Al–Hg], and quinol or *p*-$C_6H_4(NH_2)_2$ with continuous removal of the MeOH–(**III**) azeotrope. Compositions of various azeotropes of ROH with (**III**) are given. Polymerisation in emulsion gives products which increase in stickiness from (**III**) (not sticky) to (**II**); the brittle point is a min. (—65°) with (**II**). Physical data of the esters are recorded. R. S. C.

Isolation and properties of naturally occurring octadecenoic (oleic) acids. R. C. Millican and J. B. Brown (*J. Biol. Chem.*, 1944, **154**, 437—450).—Octadecenoic acids isolated by low-temp. crystallisation of the Me esters of C_{18}-acids from a no. of fats and oils have been compared with oleic acid (**I**) similarly obtained from olive oil. The acids of chicken fat and of peanut, cottonseed, corn, and linseed oils appear to be identical with (**I**). Those of lard, beef tallow, beef adrenal phosphatides, pork liver lipins, human fat, and, to a somewhat smaller extent, soya-bean and rape-seed oils appear to be mixtures of (**I**) with other isomeric acids, (**I**) being the principal component. The results appear to confirm the previously reported presence of vaccenic acids in beef fat and lard. F. R. S.

Secondary reactions of ozonolysis of the ethylenic linking. M. Stoll and A. Rouve (*Helv. Chim. Acta*, 1944, **27**, 950—961).—The observations of Rieche *et al.* (A., 1944, II, 287) are extended and confirmed. Catalytic hydrogenation of Et oleate ozonide ceases after ~70% of the theoretical quantity of gas has been absorbed. The yield of aldehydes is generally ⩾55—65% and 10—15% of acids are produced by spontaneous scission of the ozonide due to the heat of the hydrogenation or to H_2O formed in the reaction. Saturated non-aldehydic compounds are formed in 15—25% yield and include fatty acid esters. It appears that scission does not occur

exclusively between the two C atoms united by the ethylenic linking but that in small proportion the terminal C of the products may be removed. Ozonisation of brassidyl or erucyl acetate in EtOAc and hydrogenation of the ozonide followed by removal of acids and distillation, heating, or treatment of the product with boiling $NaHSO_3$ causes the development of fresh acidity and evolution of gas. The monomeric, easily reduced ozonide must therefore be accompanied by one or more peroxides not reduced by H_2. These can be the polymeric ozonides of Riecke which decompose thus: ·O·CHR·O·O·CHR′·O·CHR·O·O·CHR′·O· (R = $\cdot[CH_2]_7\cdot Me$; R′ = $\cdot[CH_2]_{12}\cdot O_2Ac$) → $Me\cdot[CH_2]_{11}\cdot OAc + CO + (CO_2) +$ $Me\cdot[CH_2]_7\cdot CO_2H(CHO) + Me\cdot[CH_2]_6\cdot Me + CO_2(CO) +$ $OAc\cdot[CH_2]_{12}\cdot CHO(CO_2H)$. Lauryl acetate has been isolated in 2—5% yield. The scheme does not explain other secondary products. The wt. of the ozonide is always > that calc. for one ethylenic linking and the sap. val. of the crude product is always > that of the original material. After hydrogenation the sap. val. remains unchanged and is unaltered by separation of the aldehydes. The sap. val. of the neutral, non-aldehydic portions has therefore been raised and from them Et *n*-nonoate and Et *ω*-acetoxytridecoate have been isolated. If the EtOAc used is free from EtOH it must itself have participated in the change, which may be expressed: $2Me\cdot[CH_2]_7\cdot CH\cdot O\cdot O\cdot CH\cdot[CH_2]_{12}\cdot OAc + 2EtOAc \rightarrow$ (—O—) $Me\cdot[CH_2]_7\cdot CHO + CO_2Et\cdot[CH_2]_{12}\cdot OAc + Me\cdot[CH_2]_7\cdot CO_2Et +$ $CHO\cdot[CH_2]_{12}\cdot OAc + 2AcOH$. Scission occurs after the introduction of O_3, during either evaporation of the solution or hydrogenation. The use of ozonolysis for determining the position of a double linking may thus give rise to error. H. W.

Ricinoleic acid derivatives.—See B., 1944, II, 271.

Physiological antioxidants. P. Gyorgy and R. M. Tomarelli (*J. Biol. Chem.*, 1944, **154**, 317—324).—$(NHMe\cdot C_6H_4\cdot N:)_2$ retards the autoxidation of linoleic acid (**I**) and synergistically enhances the antioxidant activity of rice bran extract or quinol but is ineffective with *α*-tocopherol (**II**). (**II**) is the only antioxidant tested which inhibits the oxidation of (**I**) and carotene catalysed by soya-bean lipoxidase but $NHPh_2$ has a slight activity. H. G. R.

Lipins of tubercle bacilli. LXVI. Structure of tuberculostearic acid. S. F. Velick (*J. Biol. Chem.*, 1944, **154**, 497—502).—*X*-Ray examination of the crystal structure of the amides of tuberculostearic acid (**I**) and of *dl*-*α*-methylstearic acid (**II**) gives results that are consistent with the hypothesis that (**I**), although showing no detectable optical rotation, is optically active, and support the structure of the *d*- or *l*-form of (**II**) for (**I**). F. R. S.

Preparation and pyrolysis of lactic acid derivatives. Production of β-alkoxyethyl and tetrahydrofurfuryl acrylates. M. L. Fein, W. P. Ratchford, and C. H. Fisher (*J. Amer. Chem. Soc.*, 1944, **66**, 1201—1203).—Heating 81·8% lactic acid with $OR\cdot[CH_2]_2\cdot OH$ or tetrahydrofurfuryl alcohol and a little H_2SO_4 in C_6H_6 with continuous removal of H_2O gives *β-methoxyethyl* (56%), b.p. 81—82°/6 mm., *β-ethoxyethyl* (60%), b.p. 86—87°/5 mm., *β-butoxyethyl* (81%), b.p. 109—110°/6 mm., and *tetrahydrofurfuryl lactate* (79%), b.p. 114—115°/5 mm., which are also obtained in 70, 72, 71, and 84% yield, respectively, by heating Et lactate with the appropriate alcohol and Al–Hg with continuous removal of EtOH. 1·1 mols. of Ac_2O then yield 90—95% of the corresponding *α*-acetoxypropionates, (**I**) b.p. 100—101°/7 mm., (**II**) b.p. 105—106°/6 mm., b.p. 120—121°/5 mm., and b.p. 132—133°/7 mm., respectively. When passed as vapour through a Pyrex glass tube at 475—525°, these give $OMe\cdot[CH_2]_2$ (47·5%; yields in this reaction are quoted per mol. of reacted ester and are max.), b.p. 56°/12 mm., $OEt\cdot[CH_2]_2$ (40%), b.p. 77°/19 mm., $OBu\cdot[CH_2]_2$ (34%), b.p. 80°/6 mm., and tetrahydrofurfuryl acrylate (**III**) (70%), b.p. 87°/9 mm. (all obtained also by trans-esterification), with larger amounts of AcOH; (**II**) yields also 20—50% of MeCHO; (**I**) yields also 20% of MeCHO and 30% of MeOH. Thus, *β*-OR does not stabilise Et acrylate. The stability of (**III**) may be due to only one *β*-H being present in the alcohol component (cf. Claborn, U.S.P. 2,229,997; B., 1942, II, 55). Physical consts. of the esters are recorded. R. S. C.

Preparation, tautomerism, and reactions of γ-chlorinated acetoacetic ester. F. Arndt, L. Loewe, and L. Capuano (*Rev. Fac. Sci. Istanbul*, 1943, **8**, **A**, 122—152).—$CCl_3\cdot CHO$ is condensed with $CH_2(CO_2H)_2$ in boiling AcOH to $CCl_3\cdot CH(OH)\cdot CH_2\cdot CO_2H$, the Et ester, m.p. 55—56°, of which is partly oxidised by CrO_3 in AcOH containing $KHSO_4$ or $K_2S_2O_7$ at room temp. The product is extracted with Et_2O and the extract is shaken with 20% NH_3, which is immediately acidified, thus giving crude *Et γγγ-trichloroacetoacetate* (**I**), b.p. 91·5°/2·5 mm., which is purified through the *Cu* salt, m.p. 88·5 with darkening and then 92—93°. The b.p. does not remain const. when (**I**) is kept. (**I**) gives a dark red colour with $FeCl_3$ and is decomposed by NaOH with formation of $CHCl_3$. *Me γγγ-trichloroacetoacetate* (**II**), b.p. 77°/2·5 mm., 89—90°/4 mm. [*Cu* derivative, m.p. 156—157° (decomp.), softens at 110—112°], is obtained similarly, $CH_2Cl\cdot CO\cdot CH_2\cdot CO_2Et$ (**III**), b.p. 81—82°/3·5 mm., 103°/12 mm. (Cu derivative, m.p. 160°, decomp. 169°), and the corresponding Me ester (**IV**), b.p. 85°/4 mm., are described. (**I**) is stable to steam and hence can be kept when pure whereas (**II**) is hygroscopic and readily yields a cryst. *hydrate* (**V**), m.p. 65—67° (indef.), softens at 58°, and loses H_2O at ~115°, whereby the difference between ketonic and enolic form is destroyed. Hydrates are not formed by (**I**) or (**II**). (**I**), (**II**), (**III**), and (**IV**) are sol. in dil. alkali and dil. NH_3 whilst (**I**) and (**II**) dissolve also in Na_2CO_3; all the alkaline solutions are unstable. The indirect Br titration method of Meyer is not applicable to chlorinated acetoacetic esters, which liberate I from acidified KI without intermediate use of Br. The direct titration method shows that the proportion of enol is greater in (**III**) than in (**IV**) and greater in either than in $CH_2Ac\cdot CO_2Et$. (**III**) does not give a sharp end-point but the proportion of enol in the undiluted material is > that in (**III**). Br is very slowly decolorised by (**V**). In EtOH (**IV**) appears to exist as an equilibrium mixture of ketone, enol, and their common acetal. (**III**) and (**IV**) react more vigorously than $CH_2Ac\cdot CO_2Et$ with CH_2N_2; (**I**) and (**II**) when nearly anhyd. react violently and hence are pronouncedly acidic. With (**III**) and (**IV**) the products contain about equal proportions of the enol Me ether and ethylene oxide, the acidifying action of CH_2Cl being balanced by the electromeric action of the *I* effect. With (**I**) and (**II**) the acidifying action of CCl_3 dominates to such an extent that the product is almost exclusively enol ether practically free from the ethylene oxide. $CCl_3\cdot CH(OH)_2$ and $CHN_2\cdot CO_2Et$ at 100° give (**I**) and Et *γγγ*-trichloroglycidate (**VI**), b.p. 115—116°/11 mm., in the ratio 1 : 10. (**VI**) is unchanged by fuming, aq. HCl but is transformed by HCl–EtOH into the *chlorohydrin*, b.p. 122°/6 mm. H. W.

Condensations. Carboxylation and carbethoxylation of (XXIV) ketones, (XXV) esters, using sodium triphenylmethide reagent. (XXIV) β-Keto-ester synthesis. (**XXIV**) E. Baumgarten, R. Levine, and C. R. Hauser. (**XXV**) E. Baumgarten and C. R. Hauser (*J. Amer. Chem. Soc.*, 1944, **66**, 862—865, 1037—1038; cf. A., 1944, II, 213).—XXIV. $COBu^{\beta}_2$ with CPh_3Na at 0° and then Et_2CO_3 at room temp. gives $COBu^{\beta}\cdot CHPr^{\beta}\cdot CO_2Et$ (50%), but COMeEt with CPh_3Na and then $p\text{-}C_6H_4Ph\cdot O\cdot CO\cdot OEt$ (**I**) gives only $COEt\cdot CH{:}CMeEt$. Carboxylation of CORR′ is effected by interaction with CPh_3Na and then solid CO_2 in N_2, followed by esterification by CH_2N_2. Thus, COMeEt gives *Me β-keto-*n*-valerate* (37%), b.p. 73—76°/16 mm. (Cu salt, m.p. 160·3—160·9°), which with $NHPh\cdot NH_2$ in AcOH gives 1-phenyl-3-ethyl-5-pyrazolone and with NaOMe–$Bu^{\alpha}Br$–MeOH at 60° gives *Me α-propionyl-*n*-hexoate* (47%), b.p. 108—112°/16 mm., whence H_2SO_4–AcOH yields $n\text{-}C_5H_{11}\cdot COEt$. Pinacolone gives similarly *Me β-keto-γγ-dimethyl-*n*-valerate* (57%), b.p. 82—84°/17 mm., $COPr^{\beta}_2$ gives *Me β-keto-ααγ-trimethyl-*n*-valerate* (55%), b.p. 94—96°/26 mm., and $COBu^{\beta}_2$ gives *Me β-keto-δ-methyl-α-iso*propyl-n*-hexoate* (42%), b.p. 114—116·5°/19 mm. In general, when using CPh_3Na, the latter method is preferable to direct carbethoxylation.

XXV. By carboxylation in presence of CPh_3Na and then hydrolysis, $Pr^{\beta}CO_2Et$ gives $CMe_2(CO_2H)_2$ (**II**) (73%), m.p. 193—194° (decomp.) (lit. 192—193°), and EtOAc gives $CH_2(CO_2H)_2$ (**III**) (34%); without hydrolysis, $Pr^{\beta}CO_2Bu^{\gamma}$ gives *Bu*$^{\gamma}$ *H dimethylmalonate* (**IV**) (81%), m.p. 80·0—80·9°, and $Bu^{\gamma}OAc$ gives *Bu*$^{\gamma}$ *H malonate* (**V**) (57%), decomp. when distilled. At 140—150°, (**IV**) gives $CMe_2{:}CH_2$, (**II**), and some $Pr^{\beta}CO_2H$; at 120° (**V**) gives (**III**). In presence of CPh_3Na, EtOAc and Et_2CO_3 give $CH_2(CO_2Et)_2$ (41%) and $CH_2Ac\cdot CO_2Et$ (12%); $Pr^{\beta}CO_2Et$ and (**I**) give $CMe_2(CO_2Et)_2$ (83%); $Bu^{\gamma}OAc$ and (**I**) give $CO_2Et\cdot CH_2\cdot CO_2Bu^{\gamma}$ (25%). R. S.

Induced oxidation of oxalic acid by dichromate with ferrous sulphate as indicator.—See A., 1944, I, 253.

Emetic [antimony] derivatives of oxalic and glyoxylic acids. Y. Volmar and G. Gœttelmann (*Compt. rend* 1943, **216**, 828—8.8). $H_2C_2O_4$ and $CHO\cdot CO_2H$ unite with Sb_2O_3 to form antimonyl derivatives; those from $H_2C_2O_4$ are difficult to purify and exhibit a tendency to crystallise with one or more mols. of $H_2C_2O_4$ or normal oxalate. The products from $AcCO_2H$ and $CHO\cdot CO_2H$ are less easy to prepare and are more hydrolysable. The following are described: $SbHC_2O_5$; $SbK_2H(C_2O_4)_3,2H_2O$; $SbK(C_2O_4)_2,H_2O$; $SbK_3H_2(C_2O_4)_3,4H_2O$. H. G. R.

Purification of maleic anhydride.—See B., 1944, II, 246.

New type of active (partial) racemates. A. Fredga (*Arkiv Kemi, Min., Geol.*, 1944, **18**, **B**, No. 4, 7 pp.).—The possibility is indicated that, in some circumstances, an optically active compound may form a racemic-like mol. compound with an inactive compound of similar structure but without centres of asymmetry. An example is found in the system (+)-dimethylglutaric–glutaric acid (**I**). The m.p. curve of (**I**) with *r*- or *meso*-dimethylglutaric acid is of the ordinary eutectic type. H. W.

Formation of ketobutyrolactone carboxylic esters (ketoparaconic esters) and the mechanism of reaction of ketolisation of oxalacetic ester. H. Gault and R. Durand (*Compt. rend.*, 1943, **216**, 850).—*Et α-keto-γ-butyrolactone-β-carboxylate* (**I**), m.p. 108° (*phenylhydrazone*, m.p. 142·5°; *semicarbazone*, m.p. 209°), is obtained from $CO_2Et\cdot C(OK){:}CH\cdot CO_2Et$ (**II**) and excess of 35% CH_2O at —1°. Similarly prepared from MeCHO is the *γ-Me* derivative of (**I**),

oil (*phenylhydrazone*, m.p. 130°). A mechanism is suggested whereby RCHO [as $CHR(OH)_2$] yields an adduct with (**II**), followed by loss of H_2O + EtOH. The above results show that AlkCHO react similarly to ArCHO. A. T. P.

Trihydroxy*iso*butyric acid and its derivatives. H. M. Coleman [with J. W. E. Glattfeld] (*J. Amer. Chem. Soc.*, 1944, **66**, 1183—1188).—97% conversion of glycerol into $CO(CH_2{\cdot}OH)_2$ (**I**) (crystallo-optical properties described) by *Acetobacter suboxydans* at pH 6·0—6·8 is detailed, the reaction being followed by treatment of samples with HIO_4 and back-titration thereof. Gradually adding NaCN to (**I**) in HF, concn. to a syrup, and then hydrolysing by aq. HCl at 0° gives $(OH{\cdot}CH_2)_2C(OH){\cdot}CO_2H$ (**II**) (84%), m.p. 117° ($NHPh{\cdot}NH_2$, m.p. 121—122°, and *p-toluidine* salt, m.p. 126·5—127°), isolated by way of the basic Ba, BaX·OH, and then the Ca, $+4H_2O$, salts. With BzCl–C_5H_5N at 0°, (**II**) gives the *'-dibenzoate*, m.p. 137° [$NHPh{\cdot}NH_2$ (?) salt, m.p. 110°], but at 130—135° gives the tribenzoate [$NHPh{\cdot}NH_2$ (?) salt, m.p. 137—137·5° (red)], and with AcCl at 65° gives the *triacetate*, a resin [$NHPh{\cdot}NH_2$ (?) salt, $2(OAc{\cdot}CH_2)_2C(OAc){\cdot}CO_2H,3NHPh{\cdot}NH_2$, m.p. 94° (red)], but by heating in Ac_2O at 100° and distilling at 200—240° (bath)/1 mm. yields a *dimer*, m.p. 86—86·5°, of (?) tetra-acetoxymethylglycolide. R. S. C.

Autoxidation of ascorbic acid in presence of copper.—See A., 1944, I, 253.

Autoxidation of ascorbic acid in presence of vanadic acid, molybdic acid, and tungstic acid sols.—See A., 1944, I, 253.

Preparation of fully acetylated aldonic acids and nitriles. K. Ladenburg, M. Tishler, J. W. Wellman, and R. D. Babson (*J. Amer. Chem. Soc.*, 1944, **66**, 1217—1218).—d-*Ribonic acid tetra-acetate* (**I**), m.p. 139—140°, $[\alpha]_D^{26}$ −27·5° in AcOH, is obtained by HCl–Ac_2O in the stated yields from Cd (85%), NH_4 (46%), K (25%), Ca (22%), and Ba (4%) *d*-ribonate. Cd arabonate similarly gives 86% of *d*-arabonic acid tetra-acetate. K ribonate and AcOH at 60° give d-*ribonic acid*, m.p. 112—113°, $[\alpha]_D^{25}$ −17·3° in MeOH, unstable at room temp., which by the method of Robbins *et al.* (A., 1940, II, 266) gives (**I**) (15%), d-*ribolactone triacetate* (**II**) (10%), m.p. 54—56°, $[\alpha]_D^{25}$ +27° in $CHCl_3$, and an oil. With HCl–Ac_2O at 50° *d*-ribolactone gives (**II**) (88%). *d*-Ribonamide tetra-acetate and $POCl_3$ in boiling $CHCl_3$ give d-*ribononitrile tetra-acetate*, m.p. 71—72°, $[\alpha]_D^{25}$ +34·45° in $CHCl_3$. d-*Arabononitrile tetra-acetate*, m.p. 120—121°, $[\alpha]_D^{25}$ −3·5° in $CHCl_3$, and *d*-gluconononitrile penta-acetate are similarly prepared. R. S. C.

Salts of galacturonic acid and their application to the preparation of galacturonic acid from pectic substances. H. S. Isbell and H. L. Frush (*J. Res. Nat. Bur. Stand.*, 1944, **32**, 77—94).—Neutralisation of galacturonic acid (**I**) with the corresponding carbonate or hydroxide gives *Na*, $[\alpha]_D^{20}$ +36·0°, *K* (+0·5H_2O), $[\alpha]_D^{20}$ +31·6°, NH_4 (+0·5H_2O), $[\alpha]_D^{20}$ +35·5°, *Cd* (+2H_2O), $[\alpha]_D^{20}$ +28·4°, and *Ag* (+0·5H_2O), $[\alpha]_D^{20}$ +25·1°, *β-galacturonates* and *Ca* (+H_2O) (**II**), $[\alpha]_D^{20}$ +36·8°, and *Sr* (+5H_2O), $[\alpha]_D^{20}$ +29·1°, *α-galacturonates*. Neutralisation of (**I**) with the correct proportions of the carbonates and/or hydroxides affords *Na Ca* (+6H_2O) (**III**), $[\alpha]_D^{20}$ +32·4°, *Na Sr* (+6H_2O), $[\alpha]_D^{20}$ +30·2°, and *K Ca* (+6H_2O), $[\alpha]_D^{20}$ +31·4°, *α-galacturonates*. (**III**) treated with enough $H_2C_2O_4$ to ppt. Ca followed by the corresponding carbonate gives *Na Ba* (+6H_2O), $[\alpha]_D^{20}$ +27·8°, *Na Cd* (+6H_2O), $[\alpha]_D^{20}$ +27·3°, and *Na Pb* (+6H_2O), $[\alpha]_D^{20}$ +29·0°, *α-galacturonates*. All $[\alpha]_D$ vals. are at equilibrium in H_2O. Mutarotation studies are used to assign the configurations. (**II**) and (**III**) are recommended for the isolation of (**I**) from pectic substances. D. G.

Dimethyl dimethylene-*l*-idosaccharate. W. G. M. Jones and L. F. Wiggins (*J.C.S.*, 1944, 363).—*l*-Iditol (from *l*-sorbose with H_2–Raney Ni) oxidises (HNO_3) to *l*-idosaccharic acid, isolated as Ca salt. This, with paraformaldehyde and H_2SO_4 followed by MeOH, yields Me_2, dimethylene-*l*-idosaccharate, m.p. 296°, identical with that from epimerisation of Me_2 dimethylene-*d*-gluco- and -*d*-manno-saccharate. D. G.

Structure of monomethylene-*d*-glucosaccharolactone. W. G. M. Jones and L. F. Wiggins (*J.C.S.*, 1944, 364—366).—αγ-Monomethyleneglucosaccharo-βε-lactone on oxidation (CrO_3 in AcOH) and esterification yields *Me₂ αγ-monomethylenexylotrihydroxyglutarate* (**I**), m.p. 204°, identical with that obtained from *d*-xylose by oxidation HNO_3) to Ca xylotrihydroxyglutarate, condensation with paraformaldehyde, and esterification. (**I**) yields the free *i*-acid, m.p. 253—254°, and the diamide, m.p. 286° (negative Weerman test for α-OH), and on methylation (MeI and Ag_2O) affords *Me₂ β-methyl-αγ-monomethylenexylotrihydroxyglutarate*, m.p. 157°, giving the *diamide*, m.p. 295° (decomp.), with NH_3 in MeOH. Me_2 monomethyleneglucosaccharate gives (MeI and Ag_2O) *Me δ-methyl-αγ-monomethyleneglucosaccharo-βε-lactone*, m.p. 149° and *Me₂ βδ-dimethyl-αγ-monomethyleneglucosaccharate*, m.p. 96—97°. D. G.

Formation of " active racemates " between organic compounds of sulphur and selenium. A. Fredga (*Arkiv Kemi, Min., Geol.*, 1944, **A**, No. 17, 15 pp.).—*r*-Thioacetic-α-propionic acid (**I**), from CHMeBr·CO_2H and SH·$CH_2{\cdot}CO_2H$, has m.p. 87—88°. Reduction of (−)-(S·CHMe·$CO_2H)_2$ by Na–Hg and treatment of the product with $CH_2Cl{\cdot}CO_2Na$ gives (−)-thioacetic-α-propionic acid (**II**), m.p. 79—80°, $[\alpha]_D^{25}$ −172·9° in EtOAc (cf. Fitger, *Diss., Lund*, 1924). The corresponding (+)-*acid* (**III**) has m.p. 79—80°, $[\alpha]_D^{25}$ +172·7° in EtOAc, +173·3° in AcOH, +169·6° in abs. EtOH, +153·0° in $COMe_2$, +95·0° in $CHCl_3$, +109·8° in 0·4N-HCl, and +55·0° in neutral aq. solution. *r*-Thio-αβ-dipropionic acid, m.p. 72—72·5°, is obtained from SH·CHMe·CO_2H and $Cl{\cdot}[CH_2]_2{\cdot}CO_2H$. Reduction of $(S{\cdot}CHMe{\cdot}CO_2H)_2$ by Na–Hg and treatment of the product with $Cl{\cdot}[CH_2]_2{\cdot}CO_2H$ affords (+)-*thiodi-αβ-propionic acid* (**IV**), $[\alpha]_D^{25}$ +131·1° in EtOAc, +129·7° in AcOH, +129·2° in abs. EtOH, +125·2° in $COMe_2$, +111·1° in $CHCl_3$, +104·4° in 0·4N-HCl, +69·6° in neutral aq. solution. The similarly prepared (−)-*acid* (**V**) has $[\alpha]_D^{25}$ −131·0° in EtOAc. r-*Selenoacetic-α-propionic acid* (**VI**), m.p. 65—66°, is obtained by the successive action of Na–Hg and CHMeBr·CO_2H on $(Se{\cdot}CH_2{\cdot}CO_2H)_2$ or of Na–Hg and $CH_2Cl{\cdot}CO_2H$ on $(Se{\cdot}CHMe{\cdot}CO_2H)_2$. The (+)-*acid* (**VII**), obtained by successive treatments of (+)-$(Se{\cdot}CHMe{\cdot}CO_2H)_2$ with Na–Hg and $CH_2Cl{\cdot}CO_2H$ has m.p. 60·5—61·5°, $[\alpha]_D^{25}$ +149·4° in EtOAc, +166·2° in AcOH, +150·4° in abs. EtOH, +137·1° in $COMe_2$, +123·7° in $CHCl_3$, +116·4° in 0·4N-HCl, and +40·7° in neutral aq. solution. r-*Seleno-αβ-dipropionic acid* (**VIII**), m.p. 72·5—73·5°, is obtained by reduction of $(Se{\cdot}[CH_2]_2{\cdot}CO_2H)_2$ in presence of neutralised CHMeBr·CO_2H but not through $(Se{\cdot}CHMe{\cdot}CO_2H)_2$ and β-halogenopropionic acids. It is best resolved into its optical components by quinine in aq. $COMe_2$, thus leading to the (−)-*acid* (**IX**), two forms, m.p. 53·5—54·5° and 61·5—62·5°, $[\alpha]_D^{26}$ −124·2° in EtOAc, −121·0° in AcOH, −121·4° in abs. EtOH, −119·3° in $COMe_2$, −110·5° in $CHCl_3$, −109·6° in 0·4N-HCl, and −52·3° in neutral aq. solution (*quinine* salt, +3·33° in H_2O). M.p. diagrams show that (**I**) and (**VI**) are true racemates. (**III**) and (**VII**) give an almost rectilinear m.p. curve indicating isomorphism whilst (**II**) and (**VII**) give an active racemate. (**I**) and (**VI**) do not give a completely isomorphous series but probably a sequence of isodimorphous mixed crystals. (**IV**) and (**IX**) doubtless give an active racemate but observations are impeded by the occurrence of (**IX**) in two cryst. forms. (**VIII**) and the corresponding S acid, (**V**), and (**IX**) show extensive, possibly complete miscibility in the solid phase. H. W.

Catalytic formation of long-chain aldehydes.—See B., 1944, II, 272.

Carbonyl reduction by thioacetal hydrogenolysis. M. L. Wolfrom and J. V. Karabinos (*J. Amer. Chem. Soc.*, 1944, **66**, 909—911).—A general method is described for converting CO into CH_2 by conversion (by EtSH, $ZnCl_2$, and NaOH at 5°—room temp.) into $>C(SR)_2$, followed by hydrogenation of the crude products in presence of Raney Ni in boiling 70% EtOH. It is applied to 3 sugar acetates, 1 free sugar, and 5 other CO-compounds. Thus are obtained 1-deoxy-*D*-galactitol [*L*-fucitol] penta-acetate (66% from *D*-galactose penta-acetate), 1-deoxy-*D*-glucitol [1-deoxy-*l*-sorbitol, *L*-gulomethylitol] penta-acetate (60% from *D*-glucose penta-acetate), 2-deoxy-*D*-mannitol [-*l*-sorbitol, -*D*-glucitol] penta-acetate (20% from *D*-fructose penta-acetate), 1-deoxy-*D*-galactitol (24% from *D*-galactose), PhMe (65% from PhCHO), PhEt (66% from COPhMe), n-C_7H_{15} (50% from $COMe{\cdot}C_5H_{11}$-n and 40% from n-$C_6H_{13}{\cdot}CHO$), and CH_2Ph_2 (77% from $COPh_2$). MeCHO is isolated from the reaction mixture after reduction of $C_6H_{13}{\cdot}CH(SEt)_2$. R. S. C.

Condensations. XXVI. Acylation of methyl ketones with aliphatic esters by means of sodium amide. Synthesis of β-diketones of the type, COR·CH_2·COR′. J. T. Adams and C. R. Hauser. **XXVII. Preparation of potassium triphenylmethide and its use in condensations.** R. Levine, E. Baumgarten, and C. R. Hauser (*J. Amer. Chem. Soc.*, 1944, **66**, 1220—1222, 1230—1231; cf. A., 1944, II, 211).—XXVI. Adding COMeR (1 mol.) and then $R'CO_2Et$ (2 mols.) to $NaNH_2$ (2 mols.) in Et_2O gives $CH_2(COEt)_2$ (57% with 13% of COEt·CHMe·COMe), b.p. 78—80°/30 mm. (Cu salt, m.p. 209—210°), $CH_2(COPr^{\alpha})_2$ (68%), b.p. 101—102°/2 mm. (Cu salt, m.p. 156—157°), n-*dodecane-εη-dione* (80%), b.p. 109—110°/20 mm. (Cu salt, m.p. 136—137°), *ββ-dimethyl*-n-*decane-γε-dione* (52% with some $Bu^{\alpha}CO{\cdot}NH_2$ and $COBu^{\alpha}{\cdot}CHPr^{\alpha}{\cdot}CO_2Et$), b.p. 116—119°/20 mm. (no Cu salt), *βι-dimethyl*-n-*decane-εη-dione* (76%), b.p. 115—116°/20 mm. (blue Cu salt, m.p. 157—158°), n-*tridecane-ζθ-dione* (68%), b.p. 162—164°/20 mm. (blue Cu salt, m.p. 119—120°), *ββζζ-tetramethyl*-n-*heptane-γε-dione* (28%), b.p. 96—97°/20 mm. (purple Cu salt, m.p. 197—198°), CH_2Ac_2 (54%), $COMe{\cdot}CH_2{\cdot}COBu^{\gamma}$ (43%), b.p. 70—71°/20 mm. (Cu salt, m.p. 191—192°), $COEt{\cdot}CH_2{\cdot}COBu^{\alpha}$ (70% with 2% of COMe·CHEt·COEt), b.p. 84—76°/20 mm. (Cu salt, m.p. 157—158°), and $COMe{\cdot}CH_2{\cdot}COPr^{\beta}$ (42%), b.p. 66—67°/20 mm. (Cu salt, m.p. 171—172°). 1 mol. of $NaNH_2$ gives about half these yields; a reaction mechanism to account for this is proposed.

XXVII. $CHPh_3$ and KNH_2 in liquid NH_3 give $KCPh_3$, which after replacement of NH_3 by Et_2O is used effectively for self-condensation of $Bu^{\beta}CO_2Et$ and condensation of $Pr^{\beta}CO_2Et$ with BzCl or EtI, and for conversion of COMeEt into $COEt{\cdot}CH_2{\cdot}CO_2H$. The $CHPh_3$ recovered is re-used. R. S. C.

Acetylene derivatives. XXXIII. Conversion of divinyl ketones. Addition of hydrogen chloride to ββ-dimethyldivinyl ketone. I. N.

Nazarov and T. D. Nagibina (*Bull. Acad. Sci. U.R.S.S., Cl. Sci. Chim.*, 1943, 206—215).—Addition of 1 mol. of HCl to CH_2:CH·CO·CH:CMe_2 (**I**) (b.p. 42—43°/8 mm.) yields *vinyl β-chloroisobutyl ketone*, b.p. 57—60°/8 mm. (decomp.). Addition of 2 mols. of HCl gives a *β-chloroethyl β'-chloroisobutyl ketone*, b.p. 92—94°/9 mm. (decomp.). With a 1% solution of KOH in EtOH (**I**) forms δ-ethoxy-β-methyl-Δβ-hexen-δ-one; polymerisation of (**I**) also occurs. Hydrolysis (6% H_2SO_4) of δ-methoxy-β-methyl-Δβ-hexen-δ-one yields 2 : 2-dimethyltetrahydro-4-pyrone. Addition of 2 mols. of HCl to phorone with subsequent hydrolysis yields 2 : 2 : 6 : 6-*tetramethyltetrahydro-4-pyrone*, b.p. 73—75°/17 mm. V. B.

Solubilities of high mol. wt. symmetrical normal aliphatic tertiary amines.—See A., 1944, I, 221.

Steric strain and anomalous base strength of normal aliphatic amines.—See A., 1944, I, 224.

Preparation of *sec.*- and *tert.*-amines. C. Prévost and H. C. de Mauny (*Compt. rend.*, 1943, **216**, 771—772).—$NHEt_2$ and excess of cold 33% aq. CH_2O give NEt_2·CH_2·OH, convertible by HCl in C_6H_6 into CH_2Cl·NEt_2,HCl, which with MgBuCl, MgMeI, or MgPhBr affords *n*-C_5H_{11}·NEt_2, b.p. 155°/760 mm., NEt_3, or CH_2Ph·NEt_2, b.p. 209°/755 mm. NHMe·CH_2·OH similarly leads to CH_2Ph·NHMe, b.p. 181°/760 mm. (aurichloride, m.p. 138°). A. T. P.

Preparation of diamines from keto-nitriles.—See B., 1944, II, 247.

Manufacture of *sec.* diamines.—See B., 1944, II, 248.

Reaction between amines and unsaturated compounds containing halogen attached to one of the ethylenic carbon atoms. III. Influence of a *gem*-dimethyl group. H. C. Murfitt and J. C. Roberts (*J.C.S.*, 1944, 371—373; cf. A., 1938, II, 335).—CH_2:CBr·CO_2Et (**I**) with $NHMe_2$ in EtOH gives *Et αβ-bis(dimethylamino)propionate*, b.p. 95—96°/14 mm. [*picrate*, m.p. 122—123° (decomp.); *platinichloride*, m.p. 190° (decomp.), changes at 186°], also obtained from CH_2Br·$CHBr$·CO_2Et (**II**) and $NHMe_2$. (**I**) or (**II**) and piperidine (**III**) yield (?) *Et αβ-dipiperidinopropionate*, b.p. 175—176·5°/13 mm. (no cryst. picrate). CMe_2Br·$CHBr$·CO_2Et, b.p. 112—114°/18 mm. (from CMe_2:CH·CO_2Et and Br), with NaOEt gives *Et α-bromo-ββ-dimethylacrylate* (**IV**), b.p. 88—89°/13 mm., which with (**III**) in EtOH yields impure *Et α-piperidino-ββ-dimethylacrylate*, b.p. 122—124°/18 mm. [*platinichloride*, m.p. 183° (decomp.), softens at 179°]. With $NHMe_2$ (**IV**) gives *Et α-dimethylamino-ββ-dimethylacrylate*, b.p. 76—78°/18 mm. (deliquescent *hydrochloride*). The *gem*-Me_2 thus diminishes the reactivity towards addition across the double linking. D. G.

Phosphorylcholine. E. Baer and C. S. McArthur [with, in part, D. B. Mundell] (*J. Biol. Chem.*, 1944, **154**, 451—460).—Phosphorylation of choline with $(OPh)_2POCl$ in C_5H_5N gives diphenylphosphorylcholine, isolated as the *aurichloride*, m.p. 122—123°, decomposed by Ag to *diphenylphosphorylcholine chloride*, m.p. 133—134° (?), which is catalytically hydrogenated (PtO_2) to phosphorylcholine chloride, isolated as the Ba salt. No secondary reaction products are formed. The rates of hydrolysis of phosphorylcholine (**I**) in acid at 100° and 125° and alkali at 125° are comparable with those of α- and β-glycerophosphoric acid, and glyceric acid-3-phosphoric acid. True and pseudo-choline-esterase do not hydrolyse (**I**). F. R. S.

Tri(hydroxymethyl)aminomethane derivatives. I. Polyhydroxyamines. J. S. Pierce and J. Wotiz (*J. Amer. Chem. Soc.*, 1944, **66**, 879—881).—$(OH·CH_2)_3C·NH_2$ (**I**) (4 mols.) (*hydrochloride*, m.p. 149—150°; *hydrobromide*, m.p. 133—134°) and Br·$[CH_2]_n$·Br (1 mol.) in boiling EtOH give NN′-*di-ββ′β″-trihydroxy*-tert.-*butyl-ethylene-*, m.p. 205—206°, *-propylene-αγ-*, m.p. 170—171°, and *-hexamethylenediamine dihydrobromide*, m.p. 160·5—162°. $OH·CH(CH_2Cl)_2$ (1 mol.) and (**I**) (2 mols.), best in boiling EtOH, give *β-hydroxy*-NN′-*di-ββ′β″-trihydroxy*-tert.-*butylpropylene-αγ-diamine*, an oil (*dihydrochloride*, m.p. 186—188°; *dihydrobromide*, m.p. 160—162°). $NH([CH_2]_2·OH)_2$ (**II**) (1 mol.) with epichlorohydrin (1 mol.) in EtOH at ~30° (cooling) and then (**I**) (1 mol.) in boiling EtOH gives *β-hydroxy*-NN-*di-β-hydroxyethyl*-N′-*ββ′β″-trihydroxy*-tert.-*butylpropylene-αγ-diamine dihydrochloride*, m.p. 139—141°; *β-hydroxy*-NNN′N′-*tetra-β-hydroxyethylpropylene-αγ-diamine dihydrochloride*, m.p. 98—100°, is similarly obtained by two-stage reaction with (**II**). $NHEt·[CH_2]_2·OH$ leads similarly to *β-hydroxy*-N-*ethyl*-N-*β-hydroxyethyl*-N′-*ββ β″-trihydroxy*-tert.-*butylpropylene-αγ-diamine dihydrochloride*, a syrup. $(Cl·[CH_2]_3)_2O$ (1 mol.) and (**I**) (2 mols.) in EtOH at 100° give *γγ′-di-{ββ′β″-trihydroxy*-tert.-*butylamino}*-n-*propyl ether dihydrochloride*, an oil, but $(Cl·[CH_2]_2)_2O$ (1 mol.) and (**II**) (2 mols.) in EtOH at 150° yield *4-ββ β″-trihydroxy*-tert.-*butylmorpholine hydrochloride*, m.p. 184—185°. $OH·CH_2·CH(OH)·CH_2Cl$ (1 mol.) and (**II**) (2 mols.) in boiling EtOH give *βγ-dihydroxy*-n-*propyl-ββ′β″-trihydroxy*-tert.-*butylamine hydrochloride*, a syrup; $OH·[CH_2]_2·Cl$ or $OH·[CH_2]_3·Br$ leads similarly to β-hydroxyethyl- (*hydrochloride*, a syrup) and γ-hydroxy-*n*-propyl-*ββ′β″*-trihydroxy-*tert.*-butylamine (*hydrobromide*, a syrup). Purification of the products is difficult. Many of the bases dissolve $Fe(OH)_3$, $Bi(OH)_3$, and other metal hydroxides. R. S. C.

Synthesis of β-amino-acids. IV. β-Aminononoic acid and its derivatives. V. M. Rodionov and V. A. Zvorkina (*Bull. Acad. Sci. U.R.S.S., Cl. Sci. Chim.*, 1943, 216—232).—*β-Aminobutyric acid hydrochloride*, m.p. 109·5—110·5°, is obtained from $CH_2(CO_2H)_2$ and MeCHO–NH_3 in EtOH. *β-Aminononoic acid* (**I**), m.p. 205° (*hydrochloride*, m.p. 135·5—136°; *Bz* derivative, m.p. 129·5—131°; *urethane* derivative, m.p. 80°), results in 23% yield from heptaldehyde, $CH_2(CO_2H)_2$, and NH_3 in EtOH. KCNO yields the corresponding *uraminic acid*, (**II**), m.p. 127—128°. The *amide*, m.p. 185—186°, of (**I**) is obtained through $SOCl_2$. With hot HCl (**II**) gives a mixture of n-*hexylhexa-hydropyrimidine* and *-dihydropyrimidine*. V. B.

Manufacture of β-alanine.—See B., 1944, II, 247.

Preparation of *l*-leucyl-*l*-glutamic acid anhydride. Its behaviour towards proteinases. N. Lichtenstein (*J. Amer. Chem. Soc.*, 1944, **66**, 1103—1104).—*dl*-$CHBu^{\beta}Br$·COBr (1·25 mols.) and *l*-glutamic acid (1 mol.) in aq. alkali give a solution whence crystallisation yields *l*-leucyl-*l*-glutamic acid (**I**), $[\alpha]^{14}$ +10·2° in N-HCl, converted in β-$C_{10}H_7$·OH at 170—180° into the *anhydride*, m.p. 213—215°, $[\alpha]_D$ −47·4° in 0·1N-NH_3, which in HCl regenerates (**I**) and is unaffected by a glycerol extract of pancreatin, pancreatic proteinase, or papain. R. S. C.

Configuration of valylvaline in gramicidin. H. N. Christensen (*J. Biol. Chem.*, 1944, **154**, 427—436).—Valylvaline, separated as the free dipeptide and as the Bz derivative under various conditions from gramicidin hydrolysates, is the pure optically inactive *dl* form, *d*(−)-valyl-*d*(−)-valine + *l*(+)-valyl-*l*(+)-valine, since the p-*phenylphenacyl* ester, m.p. 201°, of the Bz derivative is identical with the synthetic *r*-form. The findings indicate that no substantial quantities of the other two possible isomerides are present in the hydrolysates. Hence optically inactive valylvaline could not have arisen by racemisation. These conclusions suggest that *Bacillus brevis* joins together in gramicidin only valines of like configuration. The p-*phenylphenacyl* ester of benzoyl-*d*(−)-valyl-*l*(+)-valine and its optical enantiomorph has m.p. 141—142°; the mixed *Et* ester has m.p. 152°, whilst the *Et* ester of benzoyl-*d*(−)-valyl-*d*(−)-valine and its enantiomorph has m.p. 153°. F. R. S.

Synthesis of tyrosyltyrosyltyrosine and tyrosyltyrosyltyrosyltyrosine. A. E. Barkdoll and W. F. Ross (*J. Amer. Chem. Soc.*, 1944, 66, 951—956).—*N*-Carbobenzyloxytyrosyltyrosine (**I**), + H_2O (A., 1934, 809), with $CHMeN_2$ gives the *Et* ester (**II**), m.p. 159—160·5°. *N*-Carbobenzyloxy-*O*-acetyltyrosine Et ester (**III**) (*loc. cit.*) with H_2–Pd-black in 0·2N-HCl–EtOH gives *tyrosyltyrosine Et* ester *hydrochloride* (**IV**), m.p. 216° (decomp.), also obtained similarly from (**II**) or from tyrosyltyrosine (**V**) by HCl–EtOH at 0°. Hydrogenation of the *Me* ester (prep. by CH_2N_2–MeOH), m.p. 174—175°, of (**I**) gives *tyrosyltyrosine Me* ester *hydrochloride*, m.p. 210°. With N-NaOH and then Ac_2O–dioxan–H_2O–NaOH, (**III**) gives *N-carbobenzyloxy-O-acetyltyrosyl-O-acetyltyrosine*, m.p. 209—210°, which is converted into an oil by PCl_5, probably owing to attack on the peptide linking. The Et ester of (**V**) [prep. from (**IV**) by $NaHCO_3$ in EtOAc–H_2O] with *N*-carbobenzyloxy-*O*-acetyltyrosyl chloride (**VI**) (modified prep.) in EtOAc gives *N-carbobenzyloxy-O-acetyltyrosyltyrosyltyrosine Et* ester (**VIII**), m.p. 211°, which with, successively, H_2–Pd-black–HCl–EtOH–dioxan, $NaHCO_3$–EtOAc–H_2O, and HCl–EtOAc at 0° give *tyrosyltyrosyltyrosine Et* ester *hydrochloride* (**IX**), m.p. 231—231·5° after darkening and sintering. 1·1N-NaOH hydrolyses (**VII**) to *N-carbobenzyloxytyrosyltyrosyltyrosine*, m.p. 182—183°, whence H_2–Pd-black and a trace of AcOH in MeOH yield *tyrosyltyrosyltyrosine* (**X**), + $2H_2O$, m.p. 181—182 [with HCl–EtOH gives (**IX**)]. N_2H_4 and (**III**) in EtOH give *N-carbobenzyloxytyrosyltyrosine hydrazide*, + H_2O, m.p. 246° (decomp.), which gives only indefinite products with the Et ester of (**V**). Pure (**VI**) with (**VIII**) in EtOAc gives *N-carbobenzyloxy-O-acetyltyrosyltyrosyltyrosyltyrosine Et* ester, m.p. 235·5—236·5°, hydrolysed by N-NaOH to the *acid*, + MeOH, darkens at 220°, m.p. 224—225°, (decomp.), whence H_2–Pd-black and a trace of AcOH in MeOH yield *tyrosyltyrosyltyrosyltyrosine* (**XI**), a glass. Tyrosine (**XII**), (**V**), and (**X**) have similar absorption max. (2750, 2760, and 2765 A., respectively) but increasing $E_{max.}$ (1350, 2850, and 4160, respectively). (**XII**) is almost insol., (**V**) and (**X**) are freely sol., but (**XI**) only slightly sol. in H_2O. In EtOH or MeOH solubility increases regularly from the mono- to the tetra-peptide. (**X**) and (**XII**) give ppts. with Millon's reagent. *N-Carbobenzyloxy-O-acetyltyrosine Me* ester [prep. from the acid (**XIII**) by CH_2N_2–MeOH], m.p. 73—74·5°, with H_2–Pd-black in 0·27N-HCl–MeOH gives tyrosine Me ester hydrochloride, but in AcOH gives *O*-acetyltyrosine Me ester [*hydrochloride*, m.p. 201° (decomp.)]. Similarly, H_2–Pd-black converts (**XIII**) in AcOH into *O*-acetyltyrosine [*hydrochloride*, m.p. 223° (decomp.)]. When (**I**) or (**II**) is treated with HCl–EtOH at 0°, esterification is accompanied by partial hydrolysis of the O·CO·O·CH_2Ph, but at the b.p. both reactions are complete; these are general reactions since they occur also with *N*-carbobenzyloxyglycine and its *Et* ester, m.p. 35·5—36·5°. R. S. C.

Synthesis of methionine containing isotopic carbon and
G. W. Kilmer and V. du Vigneaud (*J. Biol. Chem.*, 1944, 154,

247—253).—$CH_2Ph·^{34}SH$, obtained from CH_2PhCl and ^{34}S (from $Na_2{}^{34}SO_3$), with $CH_2Cl·^{13}CH_2Cl$, obtained from $^{13}CH_2Me·NH_2$ (from $Na^{13}CN$), gives $CH_2Ph·^{34}S·^{13}CH_2·^{13}CH_2Cl$, converted by methods previously described into isotopic methionine, $^{34}SMe·[^{13}CH_2]_2·CH(NH_2)·CO_2H$. F. R. S.

Hydrolysis of tartaramides. M. Badoche (*Compt. rend.*, 1943, **216**, 892—895).—A mechanism is given to explain the non-racemisation of *d*-tartaramide on alkaline hydrolysis, through an intermediate enolamine. A. T. P.

Structure-chemical investigations. XIII. Malondithioamide. H. Lehr, W. Guex, and H. Erlenmeyer (*Helv. Chim. Acta*, 1944, **27**, 970—972).—$CH_2(CN)_2$ is converted by H_2S in EtOH containing KOEt at −10° and then at >50° into *malondithioamide* (**I**), m.p. 212° after decomp., converted by warm CH_2AcCl into *di-4-methyl-2-thiazolylmethane dihydrochloride*, m.p. 221° (decomp.), and by $COPh·CH_2Br$ in warm AcOH into *di-4-phenyl-2-thiazolylmethane*, m.p. 119—120°. With $(CO·CH_2Br)_2$ (**I**) gives a pale yellow, amorphous product which rapidly darkens, possibly denoting the conversion of a chain polymeride, in part at any rate, into a macrocyclic compound. H. W.

Reduction of nitroguanidine. Oxidation potentials of the nitroguanidine–nitrosoguanidine and nitrosoguanidine–aminoguanidine systems.—See A., 1944, I, 251.

Composition and constitution of ethylenebiguanide. K. Chakravarty and P. Ray (*J. Indian Chem. Soc.*, 1944, **21**, 41—43).—Attempts to prepare ethylenebiguanide from $(CH_2·NH_2)_2$,2HCl and dicyanodiamide according to Dittler (A., 1908, i, 924) give ethylenedibiguanide $[CH_2·NH·C(:NH)·NH·C(:NH)·NH_2]_2$, isolated as the *sulphate* (+1·5H_2O). Its constitution is confirmed by the isolation of the *compounds*, $C_6H_{14}N_{10}Cu,H_2SO_4,2·5H_2O$ and $C_6H_{14}N_{10}Cu,2HCl$. F. R. S.

Guanylurea salts.—See B., 1944, II, 248.

Preparation of ethyl monoalkylcyanoacetates by simultaneous condensation–reduction. E. R. Alexander and A. C. Cope (*J. Amer. Chem. Soc.*, 1944, **66**, 886—888).—Simultaneous condensation and hydrogenation (Pd–C; 1—2 atm.) of CORR′ and $CN·CH_2·CO_2Et$ gives, usually, good yields of $CRR'·CH(CN)·CO_2Et$. For aldehydes piperidine acetate and AcOH, and for ketones NH_4OAc–AcOH, are the best condensing agents. For ketones EtOH, for C_{2-4}-aldelydes AcOH, and for other aldehydes dioxan is the best solvent. Use of PtO_2 leads to reduction of CN, and Raney Ni is inactivated by the AcOH. $COPr^n_2$ gives only a 39% yield, and $COBu^\beta_2$ gives an impure product. $CH_2(CO_2Et)_2$ does not react thus. The following are new: *Et α-cyano*-n-*nonoate*, b.p. 111—113°/1 mm., *-βδ-dimethyl*-n-*hexoate*, b.p. 117—119°/8 nm., *-β-methyl*-n-*octoate*, b.p. 135—137°/8 mm., and *-β-methyl*-n-*nonoate*, b.p. 112—115°/1 mm. R. S. C.

Cleavage of (dialkylvinyl)alkylcyanoacetic esters by sodium alkoxides. E. M. Osman and A. C. Cope (*J. Amer. Chem. Soc.*, 1944, **66**, 881—886).—Cleavage of $CHR:CR'·CR''(CN)·CO_2R'''$ by NaOAlk–AlkOH at 30—80° to unsaturated nitriles and alkyl carbonates is very facile owing to the electron-attracting properties of CHR:CHR′ and CN; variation of R″ affects the results as expected from the electronic properties of R″; variation of R‴ has little effect, except that cleavage is slow when R‴ = Me. The reaction is useful for the prep. of unsaturated nitriles, which are obtained mostly in the Δ^α-form. Hydrolysis by KOH–$(CH_2·OH)_2$ gives 49—81% of mixed Δ^α- and Δ^β-acids. Cleavage of malonic ester derivatives is much slower. The following are described. *Et α-cyano-αβ-dimethyl-*Δ^β-n-*pentenoate*, b.p. 106—108°/11 mm., *α-cyano-αβδ-trimethyl-*Δ^β-n-*hexenoate*, b.p. 129—133°/20 mm., *α-cyano-α-methyl-β*-n-*propyl-*Δ^β-n-*hexenoate*, b.p. 128—129°/12 mm., and *α-cyano-αβ-dimethyl-*Δ^β-n-*octenoate*, b.p. 132—136°/12 mm.; *Me*, b.p. 114—116°/8 mm., and *α-cyano-β-methyl-α-ethyl-*Δ^β-n-*hexenoate*, b.p. 139—142°/23 mm.; *αβ-dimethyl*-n-*pentenonitrile*, b.p. 64°/17 mm., *-n-hexenonitrile*, b.p. 73—77°/14—16 mm., and *-n-octenonitrile*, b.p. 96—98°/9 mm.; *α-methyl-β-ethyl*-n-*pentenonitrile*, b.p. 74—76°/17 mm.; *β-methyl-α-ethyl-* (**I**), b.p. 76—78°/8 mm., *β-methyl-α*-n-*propyl-*, b.p. 98°/14 mm., *β-methyl-α*-iso*propyl-*, b.p. 81—84°/9 mm., *αβδ-trimethyl-*, b.p. 74—76°/9 mm., and *α-methyl-β*-n-*propyl-*, b.p. 88—90°/8 mm., *-n-hexenonitrile*; mixed *αβ-dimethyl-*, b.p. 115—118°/10 mm., *β-methyl-α*-n-*propyl-*, b.p. 131—133°/10 mm., *αβδ-trimethyl-*, b.p. 135—140°/20 mm., and *α-methyl-β*-n-*propyl*-n-*hexenoic*, b.p. 129—133°/9 mm., and *αβ-dimethyl*-n-*octenoic acid*, b.p. 137—140°/10 mm. H_2–Pd–C reduces (**I**) in EtOH to *β-methyl-α-ethyl*-n-*hexonitrile*, b.p. 71 72°/7 mm., hydrolysed, as above, to $CHMePr^\alpha·CHEt·CO_2H$, b.p. 230° (amide, m.p. 96—97°). Adding (**I**) to $NaNH_2$ in C_6H_6 (exothermal) and then boiling gives *β-methyl-α-ethyl-*Δ^α-n-*hexenoamidine* (27—53%), b.p. 99—101°/1 mm., unstable when kept (*picrate*, m.p. 136·5—137·5°). R. S. C.

II.—SUGARS AND GLUCOSIDES.

Starch. XXVII. Preparation of glucose 1-phosphate. P. Bernfeld, C. de Traz, and C. Gautier (*Helv. Chim. Acta*, 1944, **27**, 843—).—A detailed description is given of the prep. of glucose 1-phosphate, isolated as the K salt, by the enzymic phosphorolysis of starch. H. W.

Isolation of fructose 1-phosphate from biological material [liver].—See A., 1944, III, 743.

Synthesis of *DL*-threose. Preparation of *DL*-erythrose tribenzoate. W. W. Lake and J. W. E. Glattfeld (*J. Amer. Chem. Soc.*, 1944, **66**, 1091—1095).—*DL*-Threonic acid (**I**) (modified prep.) and BzCl in C_5H_5N at ≯ room temp. give DL-*threonolactone dibenzoate* (**II**), m.p. 142·5°. *K* DL-threo-*γ-chloro-αβ-dihydroxybutyrate* (prep. in EtOH) at 180—190°/0·1—0·5 mm. gives DL-*threonolactone* (**III**) (83%), b.p. 151—151·5°/0·5 mm., hydrolysed by H_2O at 70—80° to (**I**) and converted by BzCl–C_5H_5N into (**II**). By the method of Glattfeld *et al.* (A., 1935, 72), (**III**) gives DL-*threonamide*, m.p. 116°, converted by BzCl–C_5H_5N at room temp. into the *tribenzoate*, m.p. 155°. With N_2O_3 in AcOH at 15—20° this gives DL-*threonic acid tribenzoate*, *forms*, m.p. 95—98° and 121°, the *chloride* (prep. by $SOCl_2$), m.p. 113·5°, of which with H_2–Pd–$BaSO_4$ in xylene yields DL-*threose tribenzoate* (**IV**), m.p. 99—99·5° (2 : 4-*dinitrophenylhydrazone*, m.p. 182°). NaOMe–MeOH at −15° or 0·3N-$Ba(OH)_2$ at 0° hydrolyses (**IV**) to *DL*-threose, a syrup [osazone, m.p. 167—168° (darkens; bath preheated at 165°)], which is oxidised by Br to (**I**) [isolated as (**II**)]. Oily *DL*-erythronamide, similarly obtained, gives the *tribenzoate*, m.p. 208°, and thence DL-*erythronic acid tribenzoate*, m.p. 151·5—152°, the *chloride*, m.p. 103·5°, of which does not yield cryst. *DL*-erythrose. M.p. are corr. R. S. C.

Optical activity of the copper complexes of polysaccharides and substituted methylglucosides. R. R. Reeves (*J. Biol. Chem.*, 1944, **154**, 49—55).—The four methyl-*β*-methylglucopyranosides show widely different optical behaviour when dissolved in cuprammonium hydroxide solution (**I**). The optical activity of methyl-2-methyl-*β*-glucoside in H_2O and in (**I**) so closely resembles that of the polysaccharide from *Phytomonas tumefaciens* that it is suggested that this polysaccharide is composed of glucopyranose units linked chiefly through the 2 position. The optical behaviour of a 3-linked polysaccharide and several 4-linked polysaccharides is similar to that of the correspondingly substituted methylglucosides. The shift in the optical rotation of glucopyranoside polysaccharides in (**I**) may be used to classify glucose polysaccharides and furnish information regarding their structure. F. R. S.

Carbanilates of α- and β-methyl-*d*-glucosides. W. M. Hearon, G. D. Hiatt, and C. R. Fordyce (*J. Amer. Chem. Soc.*, 1944, **66**, 995—997).—α- or β-Mcthyl-*d*-glucoside 2 : 3 : 4-triacetate and PhNCO in C_5H_5N exothermally and then at 90° give α-, m.p. 147—148°, [α] +145° in $CHCl_3$, and *β-methyl*-d-*glucoside* 2 : 3 : 4-*triacetate* 1-*carbanilate*, m.p. 147—148°, [α] +15° in $CHCl_3$, respectively, hydrolysed by 0·5% HCl–MeOH at the b.p. to α-, m.p. 131—133°, [α] +115° in C_5H_5N, and *β-methyl*-d-*glucoside* 1-*carbanilate*, m.p. 144—145°, [α] −9° in C_5H_5N, respectively. 4 : 6-Benzylidene-α- and -β-methyl-*d*-glucoside gives similarly the 2 : 3-*dicarbanilates*, m.p. 216—217°, [α] +40° in $CHCl_3$, and m.p. 247—248°, [α] −50° in $CHCl_3$, hydrolysed by 0·75% HCl–MeOH at the b.p. to α-, m.p. 151—153°, [α] +55° in C_5H_5N (4 : 6-*diacetate*, m.p. 189—190°, [α] +124° in C_5H_5N), and *β-methyl*-d-*glucoside* 2 : 3-*dicarbanilate*, m.p. 219—220°, [α] −103° in C_5H_5N (4 : 6-*diacetate*, m.p. 217—218°, [α] −22° in C_5H_5N), respectively. α- and β-Mcthyl-*d*-glucoside 6-CPh_3 ether give similarly the 2 : 3 : 4-*tricarbanilates*, m.p. 229—231°, [α] +52° in $CHCl_3$, and m.p. 232—234°, [α] −5° in $CHCl_3$, hydrolysed by 1% HCl–MeOH to α-, m.p. 192—193°, [α] +84° in $CHCl_3$, and *β-methyl*-d-*glucoside* 2 : 3 : 4-*tricarbanilate*, m.p. 234·5°, [α] +6° in C_5H_5N. [α] are $[\alpha]_D^{25}$. R. S. C.

Hydrolysis of maltohexaose and the products obtained thereby, principally maltotriose. K. Myrback and E. Leissner (*Arkiv Kemi, Min., Geol.*, 1944, **17**, **A**, No. 18, 22 pp.).—The concn. of the products of the hydrolysis of maltohexaose at time *t* is calc. on the following assumptions: (*a*) that all glucosidic linkings independent of the position and no. of the saccharide linkings are attacked at the same rate, (*b*) that the glucosidic linkings of the disaccharide are attacked with a velocity k_2 and all other linkings with a different velocity k_1, (*c*) that a terminal linking of all saccharides is resolved at a rate k_1 and all other linkings at a rate k_2, (*d*) that all linkings of a saccharide with *n* units are resolved at the same rate k_n, whereby $k_n = Ck_{n+1}$; calculation is made for the special case in which $C = 1·2$. In hydrolysates of this kind the sum of monosaccharide (glucose) (**I**) + disaccharide (maltose) (**II**) is customarily determined by fermentation. In such a hydrolysate (**I**) is not determined and from its amount the concn. of the remaining hydrolytic products is calc. on the above assumptions. It is found, however, that maltotriose (**III**) in addition to (**I**) and (**II**) is fermentable. It is therefore possible that the composition of starch hydrolysates in which (**I**) and (**II**) have been determined by fermentation differs markedly from that which has been assumed. (**III**), like (**II**), is not attacked by amylase. H. W.

Sugar in the cerebroside of the spleen in Gaucher's disease.—See A., 1944, III, 755.

Constitution of the tannin from Indian teripods. H. G. Biswas (*J. Indian Chem. Soc.*, 1944, **21**, 32—34).—Extraction with EtOH

of the pod cases of *Caesalpinia digyna* yields a *tannin*, m.p. 205—212° (decomp.), which on hydrolysis yields gallic acid and glucose. Acetylation (Ac_2O–C_5H_5N at room temp.) gives a *nona-acetate*, m.p. 206—208° (decomp.). The hydrolysis data are in fair agreement with the tannin being monodigalloylglucose. C. R. H.

Catalposide, the heteroside of *Catalpa* fruits. H. Colin, G. Tanret, and (Mlle.) M. Chollet (*Compt. rend.*, 1943, **216**, 677—679).—Catalposide, softens ~160°, m.p. 165°, resolidifies, darkens at ~190°, remelts 212° (block), $[\alpha]^{15}$ −149° (anhyd.) in H_2O, is hydrolysed by H_2SO_4 or emulsin to β-*d*-glucose and an unstable aglucone. R. S. C.

Lead tetra-acetate oxidations in the sugar group. VIII. Preparation and proof of structure of *N*-acetyl-*D*-glucofuranosylamine. R. C. Hockett and L. B. Chandler (*J. Amer. Chem. Soc.*, 1944, **66**, 957—960; cf. A., 1944, II, 214).—*aldehydo-D*-Glucose pentaacetate (**I**) in 29% aq. NH_3 at 50—60° gives *acet*-D-*glucofuranosylamide* (**II**), m.p. 189—191° (decomp.), $[\alpha]_D^{22\cdot4}$ +86·7° → +85·8° in H_2O in 10 days, converted by Ac_2O–C_5H_5N at 75—80° or Ac_2O–NaOAc at 90° into the *amide tetra*-O-*acetate*, m.p. 82·5—84·5°, $[\alpha]_D$ +32·7° in $CHCl_3$, which could not be obtained from (**I**) by NH_2Ac. *D-α-Glucoheptoseoxime*, m.p. 100—101°, $[\alpha]_D$ −6·3° → 0·9° in $CHCl_3$ in 70 hr., with Ac_2O–NaOAc at 100° gives *D-α-glucoheptonitrile hexa-acetate*, m.p. 85·5—87·5° (lit. 112·5—113·5°, $[\alpha]_D^{24\cdot8}$ +24·3° in $CHCl_3$), whence 29% aq. NH_3 at 50° gives (**II**), m.p. 192—194°. With $Pb(OAc)_4$, (**II**) gives an oxidation curve of type IV with production of CH_2O. Attempts to prepare *D*-xylose diacetamide and cryst. *D*-guloseoxime or *D*-gulonitrile pentaacetate failed. The mechanism of formation of NHAc-derivatives of sugars is discussed. R. S. C.

Chemistry of tissues. I. Chondroitin from cartilage. H. G. Bray, J. E. Gregory, and M. Stacey (*Biochem. J.*, 1944, **38**, 142—146).—Chondroitin sulphate (**I**), isolated from bovine nasal septa and bovine and human trachea, is degraded and methylated to a sulphate-free product of low mol. wt. The amide of 2 : 3 : 4-trimethyl-α-methylglucuronoside and 3 : 4 : 6-trimethyl-*N*-acetyl-α-methylchondrosaminide are isolated from an acid hydrolysate. (**I**) has a branched chain structure of glucuronic acid and chondrosamine residues. Some of the glucuronic acid units are terminal groups which are combined by glycosidic linkings through their $C_{(1)}$ atom. R. L. E.

Adsorption of fatty acid by the linear component of corn starch. T. J. Schoch and C. B. Williams (*J. Amer. Chem. Soc.*, 1944, **66**, 1232—1233).—Extracting commercial maize starch with 81% aq. dioxan increases its I-affinity from 4·1—4·4% to 5·3%; the fatty acid is selectively adsorbed on the linear components (*A*), thus reducing the I-affinity. Heating 2% defatted maize starch paste (3 l.) in an autoclave, adding oleic acid (200 ml), and cooling slowly gives a 29% yield of *A* as a microcryst. floc having I-affinity 14·5% after extraction by MeOH; the non-pptd., branched chain has, after extraction, I-affinity <0·2%. The purest *A* has I-affinity 19·0%, whence it is calc. that defatted maize starch contains 28% of *A*. R. S. C.

Mol. wt. of cellulose. Measurements of average degree of polymerisation. O. A. Battista (*Ind. Eng. Chem.* [*Anal.*], 1944, **16**, 351—354).—Data on η and concn. are given for five samples of purified cellulose covering a degree of polymerisation from 300 to 3000. A plot of log η/c against c, and of the log of the relative η function at 0·5% concn. against degree of polymerisation, give straight lines. The data have been used to derive a mathematical expression by means of which the val. of the η function at 0·5% concn. may be converted to degree of polymerisation data equiv. to vals. obtained by extrapolation of η–concn. data to infinite dilution. J. D. R.

Form and mobility of cellulose molecule.—See A., 1944, I, 240.

III.—HOMOCYCLIC.

Acetylene derivatives in the C_6 alicyclic series. M. Mousseron (*Compt. rend.*, 1943, **217**, 155—157).—The optical activity of methyl*cyclo*hexane, substituted in the 3-position by groups containing C:C, is increased by the C:C (notably when distant from the ring), by the lengthening of the C side-chain (for a fixed (C:C); the *cis*- has a higher rotation than the *trans*-isomeride. The presence of an intranuclear double linking in the corresponding *cyclo*hexencs also raises the optical activity. The *cis*-, b.p. 58°/25 mm., $[\alpha]_{546}$ −6·3°, and *trans*-, b.p. 60°/25 mm., $[\alpha]_{546}$ −3·45°, -3-acctylenyl, *cis*-, b.p. 75°/25 mm., $[\alpha]_{546}$ −7·6°, and *trans*-, b.p. 77°/25 mm., $[\alpha]_{546}$ −4·45°, -Δ$^{\alpha}$-propinenyl, *cis*-, b.p. 74°/25 mm., $[\alpha]_{546}$ −8·35°, and *trans*-, b.p. 78°/25 mm., $[\alpha]_{546}$ −4·72°, -Δ$^{\beta}$-propinenyl, *cis*-, b.p. 94°/25 mm., $[\alpha]_{546}$ −11·87°, and *trans*-, b.p. 98°/25 mm., $[\alpha]_{546}$ −6·71°, -Δ$^{\beta}$-butinenyl, and *trans*-3-Δ$^{\alpha}$-, b.p. 95°/25 mm., $[\alpha]_{546}$ −5·3°, and -Δ$^{\gamma}$-, b.p. 92°/25 mm., $[\alpha]_{546}$ −7·74°, -butinenyl derivatives of methyl*cyclo*hexane are described. 1-Methyl-3-acetylenyl- and -3-Δ$^{\alpha}$-propinenyl-Δ^{3}-*cyclo*hexene have $[\alpha]_{546}$ +75·2° and +88·4°, respectively. Me 3-methyl-*cyclo*hexyl-butinenoate, b.p. 155°/25 mm., $[\alpha]_{546}$ −6·92° (free acid, $[\alpha]_{546}$ −7·63°), and -pentinenoate, b.p. 175°/25 mm. $[\alpha]_{546}$ −9·47°, are prepared. F. R. S.

Sulphonic acids of aromatic compounds.—See B., 1944, II, 274.

Sulphonation of phenylpropylenes. C. M. Suter and W. E. Truce (*J. Amer. Chem. Soc.*, 1944, **66**, 1105—1109).—Adding CPhMe:CH_2 (0·94 mol.) to dioxan (2·0), SO_3 (1·69 mols.), and $(CH_2Cl)_2$ (400 g.) at 20—25°, keeping at 5°, and adding to aq. $Ba(OH)_2$ gives *Ba β-phenylpropene-αγ-disulphonate* (reduces $KMnO_4$ and decolorises aq. Br) and thence the *di*-S-p-*chlorobenzylthiuronium* salt (**I**), m.p. 215—217°. Adding CPhMe:CH_2 (54) to SO_3 (85), dioxan (176), and CCl_4 (500 g.) at 10—15° gives the corresponding *dioxan* salt (**II**) and thence the *Na*$_2$ salt. At 0° much monosulphonic acid is also formed. Treating (**II**) with PCl_5 in $(CH_2Cl)_2$ at the b.p. and then room temp., removing HCl by H_2O, and adding liquid NH_3 gives *β-phenylpropene-αγ-disulphonamide*, m.p. 197—200°. OH·CPh$(CH_2Cl)_2$ [prep. from $CO(CH_2Cl)_2$ by MgPhBr] and Na_2SO_3 in H_2O at 100° give β-hydroxy-β-phenylpropane-αγ-disulphonic acid (*di*-S-p-*chlorobenzylthiuronium* salt, m.p. 164—166°), the *Na*$_2$ salt of which with Ac_2O at about the b.p. or with $POCl_3$–PCl_5 at 75° and then hot aq. NaOH etc. yields (**I**). CH_2Ph·CH:CH_2 with SO_3, dioxan, and $(CH_2Cl)_2$ at <20° and then aq. $Ba(OH)_2$ gives *Ba β-hydroxy-γ-phenylpropane-α-sulphonate* (**III**) (derived S-p-*chlorobenzylthiuronium* salt, m.p. 156—158°) [and a resin (see below)], which with aq. $KMnO_4$ at 100° gives BzOH, does not decolorise aq. Br, and with PCl_5–$(CH_2Cl)_2$ at 100° and then NH_3 gives *γ-phenyl-Δ$^{\alpha}$-propene-α-sulphonamide*, m.p. 65—67°. CHPh:CH·CH_2Cl (**IV**) with, successively, Na_2SO_3, PCl_5–$(CH_2Cl)_2$, and NH_3 gives *α-phenyl-Δ$^{\alpha}$-propene-γ-sulphonamide*, m.p. 126—127°. The Na_2 salt derived from (**III**) is converted by Ac_2O at 120° into *Na β-acetoxy-γ-phenylpropane-α-sulphonate* (**V**), m.p. 171—174°, which at 210—215° yields AcOH and *Na α-phenyl-Δ$^{\alpha}$-propene-γ-sulphonate* [derived S-p-*chlorobenzylthiuronium* salt (**VI**), m.p. 196—198°], also obtained from (**IV**) by Na_2SO_3. CH_2Ph·CH:CH_2 and aq. Br–KBr at 90° give CH_2Ph·CH(OH)·CH_2Br (70%), converted by Na_2SO_3 and then Ac_2O into (**V**). (**VI**) is also obtained from the resin accompanying (**III**). CHPh:CHMe with SO_3, dioxan, and $(CH_2Cl)_2$ at 15—20° and then aq. $Ba(OH)_2$ gives impure Ba α-phenyl-Δ$^{\alpha}$-propene-β-sulphonate (with $KMnO_4$ gives BzOH) and thence the *Na* (**VII**), +H_2O, m.p. ~180°, and S-p-*chlorobenzylthiuronium* salt, m.p. 162—163°. At 230° (**VII**) gives CH_2Ph·CH:CH_2 + Na_2SO_4 and with PCl_5–CCl_4 and then NH_3 gives *α-phenyl-Δ$^{\alpha}$-propene-β-sulphonamide* (**VIII**), m.p. 138—139°. CHPh.CHMe with aq. Br or HOCl gives mixtures. CHMeBr·CHPh·OH (from COPh·CHMeBr) with hot aq. Na_2SO_3 gives *Na α-hydroxy-α-phenylpropane-β-sulphonate*, decomp. >250° (derived *S*-p-chlorobenzylthiuronium salt, m.p. 184—185°), and thence by PCl_5 etc. yields (**VIII**). R. S. C.

Addition products of dienes to toluene. B. A. Arbusov and E. V. Kuznetzov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, **39**, 311—313).—Butadiene (**I**), PhMe, and finely-dispersed Na at 90°/5 atm. for 10 hr. yield an oil, b.p. 80—220°/16 mm., which affords four *adducts*, viz., from 1 mol. of PhMe and 1, 2, 3, or 4 mols. of (**I**), of b.p. 92—94°, 140—142°, 188—191°, and 210—220°, all at 16 mm., and yields (based on above oil) of 50, 27, 20, and 3%, respectively. The 1 : 1 adduct, α-phenyl-Δ$^{\gamma}$-pentene, is cyclised by 90% H_2SO_4 (method: Bogert *et al.*, A., 1929, 642) to 1-methyltetrahydronaphthalene, b.p. 153—155°/55 mm., dehydrogenated by S to 1-$C_{10}H_7$Me. The 1 : 2 adduct, ι-phenyl-Δ$^{\beta\gamma}$-nonadiene, similarly gives a hydrogenated ethylbenznaphthalene or hydrogenated methylphenanthrene, but the structure is not clear, and attempted dehydrogenation affords no pure compound. Tetrahydronaphthalene and (**I**) give 15% of an adduct, b.p. 140—142°/16 mm., probably a methylbenznaphthalene, cyclised to a substance, b.p. 148—150°/16 mm. Δ$^{\beta\delta}$-Hexadiene and PhMe with Na at 70° in an autoclave (10 hr.) give *ζ-phenyl-ε-methyl-Δ$^{\gamma}$-hexene*, b.p. 106—110°/16 mm.

Photochemical processes in aromatic compounds.—See A., 1944, I, 255.

***o*-Substituted diphenyls.** S. H. Zaheer and S. A. Faseeh (*J. Indian Chem. Soc.*, 1944, **21**, 27—28).—2-Chloro- (**I**), -bromo-, -iodo- (**II**), and -cyano- have been prepared (Sandmeyer) from 2-aminodiphenyl. An 80% yield of *o*-C_6H_4Ph·MgI is obtained from (II) and flaked Mg in boiling Et_2O–H_2. *o*-C_6H_4Ph·MgCl (32% yield) is formed from Mg and (**I**) in an evacuated sealed tube at 210—215°/6 hr. C. R. H.

Dissociation of hexa-arylethanes. XVI. Alkyl and halogen derivatives. C. S. Marvel, H. W. Johnston, J. W. Meier, T. W. Mastin, J. Whitson, and C. M. Himel (*J. Amer. Chem. Soc.*, 1944, **66**, 914—918; cf. 1944, II, 217).—*p*-Bu$^{\gamma}$ has a remarkable promoting effect on the dissociation of C_2Ar_6. The following % of dissociation in C_6H_6 are determined magnetometrically (m.p. in parentheses are those of derived *peroxides*): tetra-*m-cyclo*hexylphenyldi-*p*- (m.p. 169—170°) 39, tetra-*p-cyclo*hexyldi-*m*- 16, and di-*p-tert.*-butylphenyltetra-*m-cyclo*hexylphenylethane (m.p. 163—164·5°) 20; di-*m*- (m.p. 185—186°) 33—42 and di-*o*-tolyl- (m.p. 159—161°) 65—68, di-*m*- 38—40 and di-*o*-bromophenyl-tetra-*p-tert.*-butylphenylethane 94; diphenyltetra-*p*- 5·3—7·6, tetraphenyldi-*m*- (m.p. 173—174°) 4—diphenyltetra-m- (m.p. 169—170°) 3·9—5·5, and hexa-*p*-fluorophenylethane 3·8; [*m*-C_6H_4Me·C(C_6H_4Me-*p*)$_2$]$_2$ 2·1%. Boiling *p*-$C_6H_4Bu^{\gamma}$·CO_2H (prep. from *p*-$C_6H_4Bu^{\gamma}$·MgBr), EtOH, C_6H_6, and H_2SO_4 in a Soxhlet apparatus over $CaCl_2$ give the *Et* ester (1)

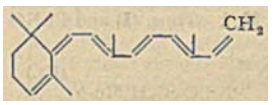
(75%), b.p. 120—120·5°/4 mm. Heating *p*-amino*cyclo*hexylbenzene and a little Zn dust in AcOH with continuous removal of H_2O gives the NHAc-compound, m.p. 129—130°, which with Fe and Br in AcOH at 30—40° (exothermic) gives 2-bromo-4-*cyclo*hexylacetanilide (71·5%), m.p. 122—123°, hydrolysed by EtOH–conc. HCl to the NH_2-compound, the hydrochloride, m.p. 207° (decomp.), of which gives (diazo-reaction; HPO_2) m-*bromo*cyclo*hexylbenzene* (**II**) (79%), b.p. 122—123°/4 mm. Adding Br to $PhBu^{\gamma}$ and a little Fe powder at 0—5° gives *p*-$C_6H_4Bu^{\gamma}Br$ (75%), b.p. 80—81°/2 mm. *p*-$C_6H_4Bu^{\gamma}\cdot NO_2$ and H_2–Raney Ni give *p*-$C_6H_4Bu^{\gamma}\cdot NH_2$, b.p. 90—93°/3 mm. Prep. as for (**II**) yields m-*bromo*-p-tert.-*butylbenzene*, b.p. 222—223°/740 mm. Grignard reaction yields m-cyclo*hexylbenzoic acid*, m.p. 120—121°; esterification as for (**I**) yields its *Et* ester, b.p. 137—139°/3 mm., and other esters required for preps. below. *m*-$C_6H_4Me\cdot MgBr$ and (**I**) give, after conversion into the Et ether, *di*-m-*tolyl*-p-tert.-*butylphenylcarbinol* (67%), m.p. 79—80°, and similar preps. yield o-*tolyldi*-p-tert.-*butylphenylcarbinol*, m.p. 129·5—130°, o-*bromophenyldi*-p-tert.-*butylphenylcarbinol*, m.p. 136·5—137°, *phenyldi*-p-*fluorophenylcarbinol*, m.p. 100°, (*p*-$C_6H_4F)_3C\cdot OH$, m.p. 94°, *diphenyl*-m-*fluorophenylcarbinol*, m.p. 117°, *phenyldi*-m-*fluorophenylcarbinol*, m.p. 114—114·5°, *tri*-m-*fluorophenylcarbinol*, m.p. 118·5—119°, and m-*tolyldi*-p-*tolylcarbinol*, m.p. 95—96°; other carbinols required for preps. below were oils. AcCl in C_6H_6 converts the appropriate carbinols into *phenyldi*-p-, m.p. 50—51°, and -m-*chlorophenyl*-, m.p. 57—59°, *di*-m-cyclo*hexylphenyl*-p-cyclo*hexylphenyl*-, m.p. 151—152°, and *di*-p-cyclo*hexylphenyl*-m-cyclo*hexylphenyl*-, m.p. 172—173°, *di*-m-cyclo*hexylphenyl*-p-tert.-*butylphenyl*-, m.p. 133—134°, *di*-m-tert.-*butylphenyl*-p-cyclo*hexylphenyl*-, m.p. 127—129°, o-, m.p. 171—172°, and m-*tolyldi*-p-tert.-*butylphenyl*-, m.p. 132—133°, o-, m.p. 135—136°, and m-*bromophenyldi*-p-tert.-*butylphenyl*-, m.p. 144—145°, *diphenyl*-m-*fluorophenyl*-, m.p. 84—84·5°, *phenyldi*-m-*fluorophenyl*-, m.p. 72·5—73°, *tri*-m-*fluorophenyl*- (prep. in EtOAc), m.p. 92—93°, *tri*-m-*chlorophenyl*-, m.p. 90—92°, and m-*tolyldi*-p-*tolyl*-, m.p. 67—69°, -*methyl chloride*. R. S. C.

Thiocarbonyls. I. Condensation of thioacetophenone with activated nickel. J. K. Cline, E. Campaigne, and J. W. Spies (*J. Amer. Chem. Soc.*, 1944, **66**, 1136—1137).—Trithioacetophenone, m.p. 121—122·1° (corr.), and Raney Ni in xylene–N_2 at 145—150° give, by "Wurtz" reaction, *trans*-$(CPhMe:)_2$ (18%) (cf. Mozingo *et al.*, A., 1943, II, 293). Cu is ineffective. R. S. C.

Synthesis of eudalene. R. N. Chakravarti (*J. Indian Chem. Soc.*, 1943, **20**, 393—398).—*o*-$C_6H_4Me\cdot CH_2\cdot CH(CO_2Et)_2$ with $CH_2Br\cdot CO_2Et$ in cold EtOH–NaOEt gives *Et* γ-o-*tolylpropane-αββ-tricarboxylate*, b.p. 186°/5 mm., which on hydrolysis and loss of CO_2 yields o-*methylbenzylsuccinic acid*, m.p. 172° (previous shrinking) (anhydride, b.p. 270°/50 mm.; *anilic acid*, m.p. 157—158°; *anil*, m.p. 114°). Cyclodehydration (H_2SO_4) then gives 1-*keto*-5-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-3-*carboxylic acid* (**I**), m.p. 164° (*semicarbazone*, m.p. 255°), reduced (Clemmensen) to 5-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-3-*carboxylic acid*, m.p. 132° [*Et* ester (**II**), b.p. 132°/4 mm.]. (**II**) with excess of MgMeI gives the 5-*methyltetrahydronaphthyldimethylcarbinol*, b.p. 145°/5 mm., dehydrogenated (Se at 230—300° for 24 hr.) to eudalene, b.p. 112°/6 mm. (styphnate, m.p. 120°). The structure of (**I**) was confirmed by independent synthesis as follows: 4-methyl-1-hydrindone [*semicarbazone*, decomp. 260°; phenylhydrazone, m.p. 139° (decomp.) (lit. 133°)] (improved prep. from β-*o*-tolylpropionic acid) with HCO_2Et in presence of Na gives the unstable 2-OH·CH: derivative, which after successive treatment with AcOH–NH_2OH,HCl at 70° and aq. EtOH–KOH gives β-3-*carboxy*-o-*tolylpropionic acid*, m.p. 172° [Et_2 ester (**III**), b.p. 150°/5 mm.]. (**III**) with Na in C_6H_6 followed by $CH_2Br\cdot CO_2Et$, and subsequent alkaline hydrolysis gave γ-3-*carboxy*-o-*tolylpropane-αβ-dicarboxylic acid*, m.p. 217—218°, the Et_2 ester, b.p. 178°/4 mm., of which yields (**I**) after treatment with Na followed by acid hydrolysis. J. N. A.

Jacobsen rearrangement. VIII. Cyclic systems. Mechanism. A. T. Arnold and R. A. Barnes (*J. Amer. Chem. Soc.*, 1944, **66**, 960—964; cf. A., 1941, II, 6).—A mechanism for the Jacobsen reaction, in which resonance plays a decisive role, is proposed. In H_2SO_4, 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydroanthracene gives 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydrophenanthrene, but 5 : 6-tetramethylenehydrindene (**I**) gives 5 : 6-benzhydrindene [2 : 3-trimethylenenaphthalene]. In H_2SO_4 2 : 3- gives 1 : 2-, but with $AlCl_3$ at 100° and then room temp. gives 1 : 3-diethyl-5 : 6 : 7 : 8-tetrahydronaphthalene, structures being proved by dehydrogenation by Pd–C at 200—240° to the appropriate $C_{10}H_6Et_2$. In H_2SO_4 5-*methyl*-6-*ethylhydrindene* (**II**) (see below) gives a 4 : 6- but with $AlCl_3$ gives a 4 : 6-dialkylhydrindene, structures being proved by oxidation. With H_2SO_4 5 : 6-*trimethylenehydrindene* (**III**) (see below) gives a tar but with $AlCl_3$ gives a 5 : 6-trimethylene-4-alkyl- and 4 : 7-dialkyl-hydrindene, structures being proved by oxidation to benzenecarboxylic acids. 5-Chloromethylhydrindene (**IV**) with Pd–$BaSO_4$ (or $–PtO_2$) in EtOH at 45—50 lb. gives 5-methylhydrindene, b.p. 86—88°/19 mm., converted by Ac_2O and $AlCl_3$ in $PhNO_2$ at 30° into 6-acetyl-5-methylhydrindene, b.p. 152—158°/11 which with HNO_3 gives 1 : 2 : 4 : 5-$C_6H_2(CO_2H)_4$ and with Zn–Hg–HCl–H_2O–AcOH gives (**II**), b.p. 112—116°/11 mm. Hydrene, $(EtCO)_2O$, and $AlCl_3$ in $PhNO_2$ give 5-*propionylhydrindene* (**V**), b.p. 159°/12 mm. (*oxime*, m.p. 95—96°). $CHNa(CO_2Et)_2$ and (**IV**) in EtOH give Et_2 5-*hydrindenylmalonate*, b.p. 158—165°/3 mm., and thence β-5-*hydrindenylpropionic acid* (91%), m.p. 82—84°, also obtained (m.p. 85—86°) from (**V**) by H_2–S–NH_3–H_2O at 150—155°. PCl_5 in C_6H_6 then yields the acid chloride, converted by $SnCl_4$–C_6H_6 into 5 : 6-*benzhydrind*-1-*one*, whence HCl–Zn–Hg–AcOH–H_2O–PhMe yields (**III**), m.p. 52—54°, b.p. 116—120°/9 mm. (**I**) gives a 4 : 7-Br_2-derivative, m.p. 141·5—142·5°. $CPhEt{:}CH\cdot CO_2Et$ with H_2–Cu chromite at 250°/2800 lb. yields $CHPhEt\cdot[CH_2]_2\cdot OH$, b.p. 145—148°/26 mm., and thence 1-keto-4-ethyl-1 : 2 : 3 : 4-tetrahydronaphthalene, which with MgEtBr–Et_2O and then Pd–C–CO_2 at 225° gives 1 : 4-*diethylnaphthalene*, m.p. 16·5—17°, b.p. 165°/25 mm. 1 : 2 : 3 : 4-Tetrahydronaphthalene with Ac_2O and $AlCl_3$ in CS_2 gives much 6-acetyl-1 : 2 : 3 : 4-tetrahydronaphthalene and some 9-acetyloctahydrophenanthrene, m.p. 50·5—51·5° (oxidised to the corresponding acid, m.p. 238—240°). Octahydroanthracene with Ac_2O and $AlCl_3$ in cold $(CHCl_2)_2$ gives the 9-*Ac* derivative, m.p. 72—72·5°, b.p. 169°/3 mm., converted by aq. KOCl into the 9-$CCl_3\cdot CO$ derivative, $+H_2O$, m.p. 123·5—124·5°. The picrate of 2 : 3-$C_{10}H_6Et_2$ has m.p. 126—128°. R. S. C.

Constitution of "cyclised" vitamin-*A*. P. Meunier, R. Dulou, and (Mlle.) A. Vinet (*Compt. rend.*, 1943, **216**, 907—908).—The following structure is assigned to "cyclised" vitamin-*A* ("axerophthene") (**I**). Vitamin-*A* and PBr_3 in C_5H_5N at 0°, then KI in boiling $COMe_2$ (method: Kuhn *et al.*, A., 1934, 395), give a compound identical in properties with (**I**), and ozonisation affords CH_2O, thus supporting the terminal CH_2. A. T. P.



Direct aromatic amination: reaction of hydroxylamine-*O*-sulphonic acid. R. N. Keller and P. A. S. Smith (*J. Amer. Chem. Soc.*, 1944, **66**, 1122—1124).—$NH_2\cdot O\cdot SO_3H$–$AlCl_3$, HN_3 in light, or HN_3–$AlCl_3$ aminates the C_6H_6 ring of aromatic compounds, the active agent being NH or NH_2^+. NH_3, N_2H_4, and/or NH_2OH are formed as by-products. $NH_2\cdot O\cdot SO_3H$–$AlCl_3$ at 95—105° converts PhMe into (mainly *p*-)toluidine (30—51%), C_6H_6 into NH_2Ph (28%), *o*-xylene into *o*-4- + *o*-3-xylidine (21%), *m*-xylene into *m*-4-xylidine (16%), *p*-xylene into *b*-xylidine (13%), PhCl into *o*- + *m*- + *p*-$C_6H_4Cl\cdot NH_2$ (2·3%), $PhNO_2$ into *m*-$NO_2\cdot C_6H_4\cdot NH_2$ (~1%), and PhOMe into $OMe\cdot C_6H_4\cdot NH_2$ (a trace). HN_3 converts PhMe in ultra-violet light at 15±2° into toluidine (a little); HN_3–$AlCl_3$ gives mixed (mainly *p*- + *o*-)toluidine; $PhNO_2$ gives, by either method, a trace of amine. $AlCl_3$ and HN_3 in $(CHCl_2)_2$ or light petroleum at room temp. give much NH_3 or N_2H_4, respectively. R. S. C.

Separation of 3-nitro-1- and 4-nitro-2-naphthylamine by maleic anhydride, and monobromination of 4-nitro-2-naphthylamine. H. H. Hodgson and D. E. Hathway (*J.C.S.*, 1944, 385—387; cf. A., 1944, II, 127).—4 : 2- (**I**), new m.p. 98·5° (*p-nitrobenzoyl*, m.p. 169°, and *azo-β-naphthol* derivative, m.p. 240°), and 3 : 1-$NO_2\cdot C_{10}H_6\cdot NH_2$ (**II**) are separated by preferential acylation of (**I**) by $(CH\cdot CO)_2O$ (**III**) to give 4-*nitro*-2-*naphthylmaleamic acid* (**IV**), m.p. 193°. Further additions of (**III**) give mixtures, followed by pure 3-*nitro*-1-*naphthylmaleamic acid*, m.p. 170°. (**IV**) is hydrolysed to (**I**) by boiling aq. EtOH–H_2SO_4. A thermal analysis diagram is constructed to determine the requisite amount of (**III**); the eutectic (73°) is 65 : 35 of (**I**) : (**II**). (**I**) is only monobrominated by >2 equivs. of Br in $CHCl_3$ to 1-*bromo*-4-*nitro*-2-*naphthylamine*, m.p. 153° (*Ac* derivative, m.p. 177°), convertible (diazo-reaction) into 1 : 4-$C_{10}H_6Br\cdot NO_2$, new m.p. 87°. 1 : 3-$C_{10}H_6(NO_2)_2$ and aq. $Na_2S_2O_4$ (≡ monoreduction) give 50% unchanged + 50% of 1 : 3-$C_{10}H_6(NH_2)_2$. A. T. P.

Phenylthiocarbamides. Contribution to the study of the triad –N·C·S–. XIV. Mechanism of desulphurisation. XV. Action of copper acetate on phenylthiocarbamide. R. Sahasrabudhey and H. Krall (*J. Indian Chem. Soc.*, 1944, **21**, 63—66, 67—70).—XIV. A new mechanism for desulphurisation is put forward. Reaction is probably initiated by the formation of mol. compounds of thiocarbamides with metal hydroxides, etc., through co-ordination at S. A second mobile H (from N to S) is essential.

XV. At ordinary temp. $Cu(OAc)_2$ with $NHPh\cdot CS\cdot NH_2$ (**I**) gives Hector's base and the simultaneously formed CuOAc forms a complex with more (**I**). In boiling solutions, desulphurisation to NHPh·CN also takes place even in presence of considerable [AcOH]. F. R. S.

Structure and activity of sulphanilamides.—See A., 1944, III, 694.

Resolution and properties of the *meso*-form of αβ-diamino-α-phenylpropane. W. Froentjes and K. M. Dijkema (*Rec. trav. chim.*, 1943, **62**, 722—728).—$NH_2\cdot CHPh\cdot CHMe\cdot NH_2$ is separated by fractional crystallisation of the Ni tetrammine perchlorates into the *meso*- (**I**), b.p. 111—112°/9 mm. (yellow salt), and *r*-form, b.p. 109—110°/9 mm. (blue salt; picrate, m.p. 233°). (**I**) is resolved by crystallisation of the *d*- and *l*-ditartrates from MeOH. The d- and l-*bases* (+2H_2O) (*sulphates*; picrates, m.p. 222°) have equal, opposite rotations in Et_2O and as ions in H_2O, but in the pure state the *d*-, *e.g.*, $[\alpha]_{5893}$ +4·2°, has a much lower val. than the *l*-form, $[\alpha]_{5893}$ −46°. Other vals. of [α] and rotatory dispersion curves are given. D. G.

Preparation and diazotisation of *p*-aminomonomethylaniline. H. H. Hodgson and E. Marsden (*J.C.S.*, 1944, 398—400).—Hantzsch's failure to diazotise *p*-$NH_2{\cdot}C_6H_4{\cdot}NHMe$ (**I**) (cf. A., 1902, i, 324) was apparently due to the presence of some *p*-$C_6H_4(NH_2)_2$, which catalyses the decomp. of diazo-compounds, and originates during the reduction of *p*-$NO{\cdot}C_6H_4{\cdot}NHMe$ (**II**) with Zn–AcOH, by fission of Me. Reduction of (**II**) or *p*-$NO_2{\cdot}C_6H_4{\cdot}NHMe$ with Fe and a little $FeSO_4$ or $Fe(NH_4)_2(SO_4)_2$ in boiling H_2O (1 hr.) gives (**I**) (*picrate*, m.p. 206°), with no rupture of Me. (**I**) is diazotised by <1 equiv. of HNO_2, added to excess of 10% aq. NaOH, unchanged (**I**) collected, and the filtrate coupled with β-$C_{10}H_7{\cdot}OH$ to give p-*methylaminobenzeneazo-β-naphthol* (**III**), m.p. 123° (*hydrochloride*, m.p. 197—202°), also obtained from *p*-$NAcMe{\cdot}C_6H_4{\cdot}N_2Cl$ and β-$C_{10}H_7{\cdot}OH$, followed by hydrolysis with boiling aq. HCl–EtOH. Similarly prepared from (**I**) and <1 mol. of HNO_2 are *p*-$C_6H_4X{\cdot}NHMe$ (X = Cl, Br); where X = I, the derivative is unstable and is converted into *p-iodo*-N-*nitrosomethylaniline*, m.p. 112°. (**I**) with >2 mols. of HNO_2, followed by alkaline β-$C_{10}H_7{\cdot}OH$, yields *p*-N-*nitrosomethylaminobenzeneazo-β-naphthol*, m.p. 178°, also obtained from (**III**) and HNO_2. A. T. P.

Azoxysulphones; preparation and properties, and observations on the structure of diazotates. W. V. Farrar and J. M. Gulland (*J.C.S.*, 1944, 368—371).—Chloramine-*T* (**I**) and ArNO yield azoxysulphones, regarded as resonance hybrids (cf. **II** and **IIa**). Thus, (**I**) and PhNO

(II.) $ArN(O)\!\rightarrow\!N{\cdot}SO_2{\cdot}C_6H_4Me\text{-}p$ $\quad\leftrightarrow\quad$ $ArN{\leftarrow}O\!=\!N{\cdot}SO_2{\cdot}C_6H_4Me\text{-}p$ (IIa.)

in C_5H_5N at room temp. for 12 hr., then at 80° for 2 hr., afford *Ph* p-*tolyl azoxysulphone* (**III**), m.p. 112—113°. Similarly (**I**) and the appropriate ArNO yield the pale yellow o-*tolyl* p-*tolyl*, m.p. 82°, *di*-p-*tolyl*, m.p. 106°, and m-*nitrophenyl* p-*tolyl*, m.p. 122·5—124°, and the bright yellow p-*phenetyl* p-*tolyl azoxysulphone*, m.p. 128—128·5°. Similarly prepared from *p*-$NO{\cdot}C_6H_4{\cdot}NAlk_2$ are p-*dimethylaminophenyl* (purple-red), m.p. 182° (decomp.), and *p-diethylaminophenyl* p-*tolyl* (bright red), m.p. 178—179° (decomp.), and *p-dimethylaminophenyl Ph azoxysulphone* (bronze), m.p. 175—176° (decomp.), which may be represented by resonance of the azoxysulphone form with a quinonoid form; in conc. acid, where hydrolysis is absent, the cation is colourless. *Ph*$_2$ *azoxysulphone* (**IV**), m.p. 123°, is obtained from $PhSO_2{\cdot}NClNa$ (chloramine-*B*) and PhNO in C_5H_5N. With (**I**), *p*-$NO{\cdot}C_6H_4{\cdot}OH$ and 5 : 1 : 2-$NO{\cdot}C_6H_3Me{\cdot}OH$ give tars, and *p*-$NO{\cdot}C_6H_4{\cdot}NH_2$ and *p*-$NO{\cdot}C_6H_3{\cdot}NHMe$ afford amorphous products of possibly complex constitution. *p*-$O{:}C_6H_4{:}O$ and (**I**) in cold EtOH give ill-defined substances. *N*-NO-compounds do not react in similar manner to the *C*-NO-derivatives. When heated alone, all monoazoxysulphone derivatives decompose violently at ~180—200°, with evolution of SO_2. *m*-$C_6H_4(NO)_2$ and (**I**) in C_5H_5N at 80° for 2 hr. yield m-*phenylene bis*-(p-*tolyl azoxysulphone*), m.p. 208° (decomp.) (darkens >200°). (**III**) and Zn–AcOH–EtOH give *p*-$C_6H_4Me{\cdot}SO_2{\cdot}NH{\cdot}NHPh$; it is attacked only slowly by boiling dil. mineral acid, acid $Na_2Cr_2O_7$, or $KMnO_4$; cold conc. HNO_3 has no action. On distilling with 50% aq. H_2SO_4, (**III**) yields PhOH; PhN_2HSO_4 is formed from (**III**) and conc. H_2SO_4 at <10°, and 1 : 2-$NPh{:}N{\cdot}C_{10}H_6{\cdot}OH$ is obtained from (**III**), 95% EtOH, β-$C_{10}H_7{\cdot}OH$, and a little 30% aq. NaOH (boil for 2 min.); (**III**) with boiling 30% aq. NaOH for 30 min. yields benzene *iso*diazotate. Thus the primary hydrolysis product of (**III**) is a *n*-diazotate. Theoretical implications of the hydrolysis, with special relation to Angeli's views on *n*- and *iso*-diozotates, are discussed. (**IV**) and conc. H_2SO_4 at 0°, followed by dilution and boiling, afford $PhSO_3H$. A. T. P.

Synthesis of iodosulphobenzeneazo- and iodocarboxybenzeneazo-derivatives of naphthol- and naphthylamine-sulphonic acids. C. J. Klemme and H. Bang (*J. Org. Chem.*, 1944, **9**, 254—258).—The dyes have been synthesised for testing as radiographic opaques. The following are obtained by coupling the requisite naphthol- or naphthylamine-sulphonic acid with diazotised 4 : 3 : 5 : 1-$NH_2{\cdot}C_6H_2I_2{\cdot}SO_3H$ or 4 : 3 : 5 : 1-$NH_2{\cdot}C_6H_2I_2{\cdot}CO_2H$: *Na*$_2$ salts of 2-(2′ : 6′-di-iodo-4′-sulphobenzeneazo)-1-naphthol-4-sulphonic acid and -1-naphthylamine-4-sulphonic acid and *Na*$_3$ salt of 2-(2′ : 6′-di-iodo-4′-sulphobenzeneazo)-1-naphthylamine-4 : 8-disulphonic acid; *Na*$_2$ salts of 2-(2′ : 6′-di-iodo-4′-carboxybenzeneazo)-1-naphthol-4-sulphonic acid and -1-naphthylamine-4-sulphonic acid and *Na*$_3$ salt of 2-(2′ : 6′-di-iodo-4′-carboxybenzeneazo)-1-naphthylamine-4 : 8-di-sulphonic acid. H. W.

Interaction of aromatic diazo-compounds with β-ketonic esters. V. V. Feofilaktov (*Bull. Acad. Sci. U.R.S.S., Cl. Sci. Chim.*, 1941, 521—530).—*n*-Valine (**I**), *n*-leucine (**II**), and *dl*-tyrosine have been prepared from Et *n*-propyl-, *n*-butyl-, and *p*-methoxybenzyl-acetoacetates and PhN_2X, the resulting α-CO-acid phenylhydrazones being reduced to the α-NH_2-acids. (**I**) and (**II**) have also been prepared using diazotates from *o*- and *p*-toluidine, *m*- and *p*-$NO_2{\cdot}C_6H_4{\cdot}NH_2$, α- and β-$C_{10}H_7{\cdot}NH_2$, and sulphanilic acid. The *p*-tolylhydrazone of *n*-butyrylformic acid occurs in two modifications, m.p. 134—135° and 123—131°. Et acetylsuccinate reacts with diazotates forming *Et* 4-*arylazo*-1-*arylpyrazol*-5-*one*-3-*carboxylates*, *e.g.*, from *o*-, m.p. 95—96°, *m*-, m.p. 146—147°, and *p*-toluidine, m.p. 143—144°, *p*-nitroaniline, m.p. 246—248°, sulphanilamide, m.p. 258—260°, naphthionic acid, benzidine. Sulphanilic acid affords up to 80% of tartrazine Et_1 ester, hydrolysed by NaOH to tartrazine (Na_3 salt). Bromotetronic acid may be used in this reaction in place of tetronic acid, forming mono- and di-arylhydrazones derived from the latter, *e.g.*, α-p-*nitrobenzeneazo*-, m.p. 214°, α-m-*tolueneazo*-, m.p. 172°, α-1-*naphthaleneazo*-, m.p. 148—150°, and α-2-*naphthaleneazo*-β-*ketobutyrolactone*, m.p. 212°. Et αγ-dibromoacetoacetate similarly affords *Et* γ-*bromo*-α-1-*naphthaleneazoaceto-acetate*, m.p. 165°. Cyclic β-ketonic esters undergo this reaction with opening of the ring. Et *cyclo*hexanonecarboxylate thus affords the *phenylhydrazone* of Et H α-ketopimelate, α-form, m.p. 89·5—90°, β-form, m.p. 142—143°, hydrolysed to α-*ketopimelic acid phenylhydrazone*, α-form, m.p. 144—145°, β-form, m.p. 131—132°. Reduction of this affords α-aminopimelic acid, m.p. 215—216°. Et *cyclo*pentanonecarboxylate similarly gives the lower homologues of these compounds. Et camphorcarboxylate gives Et 3-benzeneazo-camphor-3-carboxylate, hydrolysed to the *ketohomocamphoric acid phenylhydrazone*, m.p. 166°, reduced to α-*aminohomocamphoric acid*, m.p. 185°. 2-Cyano*cyclo*pentanone undergoes a similar reaction. G. A. R. K.

Evidence for the *iso*nitrile and nitrile structures of Hantzsch's aryl *syn*- and *anti*-diazocyanides. H. H. Hodgson and E. Marsden (*J.C.S.*, 1944, 395—398).—Although Hantzsch's formula for the *anti*-diazocyanides is correct, that for the aryl *syn*-diazocyanides does not explain the reactions. The *syn*- and *anti*-forms exhibit differences in chemical activity which are accounted for by *iso*nitrile and nitrile structures, respectively. The colours of both *syn*- and *anti*-compounds indicate covalent linkings between the diazo- and ·N:C and ·C:N groups, respectively. There is close analogy between the *syn*-diazocyanides and diazo*iso*cyanates. Temp. is of prime importance in transforming *syn*- into *anti*-diazocyanide, which occurs rapidly with the *p*-nitro- and *p*-chloro-benzene derivatives, even in Et_2O at ~0°. With *o*- and *p*-chloro- or -bromo-, and *p*-nitro-*syn*- and -*anti*-benzenediazocyanides (method of prep.: Le Fèvre *et al.*, A., 1938, II, 229), MgMeI in Et_2O affords complexes, the *anti* being of a deeper red colour than the *syn*. Decomp. with 2N-H_2SO_4 at 0° yields ~20% of MeCHO from the *syn*-complexes only, probably as follows: $C_6H_4R{\cdot}N{:}N{\cdot}N{:}C + MgMeI \rightarrow C_6H_4R{\cdot}N{:}N{\cdot}N{:}CMe{\cdot}MgI \rightarrow C_6H_4R{\cdot}N{:}N{\cdot}N{:}CHMe \rightarrow MeCHO$. The non-coupling *p*-nitrobenzenediazocarboxylamide (**I**) (stable CN linking) with Br in $CHCl_3$, AcOH, or C_6H_6 yields probably a perbromide, which readily loses Br to give p-*nitrobenzenediazo*-N-*bromocarboxylamide hydrobromide* (**II**), *p*-$NO_2{\cdot}C_6H_4{\cdot}N{:}N{\cdot}CO{\cdot}NHBr,HBr$, m.p. ~81° (decomp.). (**II**) couples with α- or β-$C_{10}H_7{\cdot}NH_2$ in $CHCl_3$ or C_6H_6 (indicates a Hofmann rearrangement), and with β-$C_{10}H_7{\cdot}OH$ in aq. EtOH or aq. NaOH (not in $CHCl_3$, C_6H_6, or abs. EtOH) (with hydrolysis to *p*-$NO_2{\cdot}C_6H_4{\cdot}N{:}N{\cdot}CO{\cdot}NH{\cdot}OH$), to give the corresponding *p*-nitrobenzeneazo-derivatives. In each case, the formation of intermediate diazo*iso*cyanate with its weak N·N linking precedes coupling. The coupling with α- and β-$C_{10}H_7{\cdot}NH_2$ in the above media supports the polarisation theory of Hodgson (A., 1943, II, 8). Aeration of (**II**) in cold H_2O for 1—1·5 hr. gives some (**I**) and the filtrate then couples with alkaline β-$C_{10}H_7{\cdot}OH$ to give 1 : NPh:N·$C_{10}H_6{\cdot}OH$. (**II**) and cold 20% aq. NaOH give 4 : 4′-dinitrodiazoaminobenzene, also obtained from *p*-$NO_2{\cdot}C_6H_4{\cdot}N_2HSO_4$ and aq. KCNO at 0°. The formation of *syn*-cyanides in mineral acid medium parallels that of diazoamino-compounds in similar media. Attempts to isolate a diazo-cyanate or -*iso*cyanate from neutral *p*-$NO_2{\cdot}C_6H_4{\cdot}N_2Cl$ with KCNO or AgCNO were unsuccessful because of the facile decomp. of the resulting diazo-compound. The views of Le Fèvre *et al.* (*loc. cit.*), with particular reference to the dipole moment data, are discussed. A. T. P.

Separation of *m*- and *p*-cresol.—See B., 1944, II, 274.

Nuclear methylation of phenolic substances. (Miss) M. G. Barclay, A. Burawoy, and G. H. Thomson (*J.C.S.*, 1944, 400—404; cf. A., 1944, II, 157).—4 : 1 : 3 : 5-$OH{\cdot}C_6H_2Me(CH_2{\cdot}OH)_2$ (**I**), distilled at >250° alone or in presence of very weak alkalis, gives much *p*-cresol (**II**), some *m*-4-xylenol (**III**), and a little mesitol (**IV**); in presence of mild alkalis, *e.g.*, $Ca(OH)_2$, $Mg(OH)_2$, borax, the amount of (**IV**) increases to 12—18% by wt. of (**I**). This reaction is characteristic of all hydroxymethylphenols and other substances capable of forming anhydrohydroxymethylphenols at high temp. The analogous behaviour of (**I**) and *p*-aminoaryl alcohols (*loc. cit.*) is shown by the formation of anhydrides, which then undergo disproportionation to yield methylated phenols and amines, respectively, and oxidised resins serving as a source of H; both also condense to a varying degree, controlled by the presence of alkalis, to form substances of high mol. wt. containing CH_2 linkings, which decompose to form mainly the original phenol or amine. Distillation of 4 : 1 : 3-$OH{\cdot}C_6H_3Me{\cdot}CH_2{\cdot}OH$ or of 3-piperidinomethyl-*p*-cresol with $Ca(OH)_2$ yields mainly (**III**), and a little (**II**) + (**IV**). Distillation of $CH_2(C_6H_3Me{\cdot}OH\text{-}5 : 2)_2$ with Na_2CO_3 gives almost pure (**II**), but with $Ca(OH)_2$ yields mainly (**II**) and a little (**III**) + (**IV**), a similar mixture also being obtained from 4-hydroxy-3 : 5-bis-(6-hydroxy-m-

methylbenzyl)toluene in presence of Na_2CO_3 or $Ca(OH)_2$. $CH_2(C_6H_3Me{\cdot}OH\text{-}5:4)_2$ and Na_2CO_3 or $Ca(OH)_2$ afford mainly *o*-cresol and traces of (**IV**). $CH_2[C_6H_2Me(OH){\cdot}CH_2{\cdot}OH\text{-}5:4:3]_2$ (**V**), m.p. 163° [prep. from *o*-cresol (1 mol.), NaOH (1·25 mols.), and aq. CH_2O for 1 week], distilled alone gives *o*-cresol, (**III**), *m*-2-xylenol (**VI**), and traces of (**IV**), but in presence of $Ca(OH)_2$ much (**III**), (**VI**), and (**IV**), with only a little *o*-cresol. 2 : 1 : 3 : 5-$OH{\cdot}C_6H_2Me(CH_2{\cdot}OH)_2$, m.p. 94°, gives, in presence of $Ca(OH)_2$, (**III**) + (**VI**) and a little (**IV**); the yield of (**IV**) is small owing to condensation to (**V**). 3 : 5-Dimethyl-2-piperidinomethylphenol with $Ca(OH)_2$ yields *m*-5-xylenol, 2 : 3 : 5 : 1-$C_6H_2Me_3{\cdot}OH$ (**VII**), and a little 2 : 3 : 5 : 6 : 1-$C_6HMe_4{\cdot}OH$ (**VIII**). 1 : 3 : 5 : 2 : 6-$OH{\cdot}C_6HMe_2(CH_2{\cdot}OH)_2$ with $Ca(OH)_2$ gives mainly (**VII**) + (**VIII**); no trace of 3 : 4 : 5-tri-, 2 : 3 : 4 : 5-tetra-, or penta-methylphenol was found, suggesting that these substances are not *p*-substituted derivatives of *m*-5-xylenol (cf. Caldwell *et al.*, A., 1939, II, 523). Distillation of 1-piperidinomethyl-2-naphthol gives β-$C_{10}H_7{\cdot}OH$ + 1 : 2-$C_{10}H_6Me{\cdot}OH$ (**IX**), the yield of (**IX**) being higher in presence of $CaCO_3$, whereas $Ca(OH)_2$ decreases the amount of β-$C_{10}H_7{\cdot}OH$ and (**IX**); traces of 1-$C_{10}H_7Me$ (**X**) are isolable. 2 : 2′-Dihydroxy-1 : 1′-dinaphthylmethane distilled alone or with Na_2CO_3 or $Ca(OH)_2$, yields much β-$C_{10}H_7{\cdot}OH$ and <2% of (**IX**) + (**X**). A mixture of phenolic substances forming a mixture of hydroxymethyl- or aminomethyl-phenols can be used: thus condensation of (**II**), CH_2O, and $Ca(OH)_2$ and distillation gives (**III**), (**II**), and (**IV**); the mixture on similar condensation and distillation affords 30% of (**IV**). Similarly (**IV**) is obtained from *o*-cresol and PhOH, a 20% yield of 2 : 3 : 4 : 6 : 1-$C_6HMe_4{\cdot}OH$ (**XI**) from *m*-cresol, and 30% of (**VIII**) from *m*-5-xylenol. A mixture of (**IV**) and (**XI**) results on similar treatment of the cresylic acids. A. T. P.

Relation of œstrogenic activity to structure in 4 : 4′-dihydroxydiphenylmethanes. E. E. Reid and (Miss) E. Wilson (*J. Amer. Chem. Soc.*, 1944, **66**, 967—969).—The appropriate ketone (1 mol.) and PhOH (3 mols.) in conc. HCl at room temp. (1 day to 20 weeks) or faster with gaseous HCl give ~90% of *ββ-di*-p-*hydroxyphenyl*-n-*heptane*, m.p. 101° (*dibenzoate*, m.p. 118°), *-octane*, m.p. 88° (*dibenzoate*, m.p. 114°), and *-γ-methylbutane*, m.p. 194° (*dibenzoate*, m.p. 204°), *ζζ-di*-p-*hydroxyphenyl*-n-*undecane*, m.p. 148·5° (*dibenzoate*, m.p. 94°), 1 : 1-di-*p*-hydroxyphenyl-4-methyl*cyclo*hexane, m.p. 179° (dibenzoate, m.p. 149·5°), *αα-di*-p-*hydroxyphenyl*-α-p-*anisylethane*, m.p. 245° (*dibenzoate*, m.p. 221°), $(p\text{-}OH{\cdot}C_6H_4)_2C(CH_2Ph)_2$, m.p. 193° (dibenzoate, m.p. 223°), and [from $(CH_2Ac)_2$] $[(p\text{-}OH{\cdot}C_6H_4)_2CMe{\cdot}CH_2]_2$, m.p. 302° (decomp.) (tetrabenzoate, m.p. 247°). Œstrogenic activity of the series, $(p\text{-}OH{\cdot}C_6H_4)_2CRR'$ is a max. at R = R′ = Pr$^\alpha$ in contrast to the stilbene series (Campbell, A., 1941, II, 62).
R. S. C.

Dibenzfuran. XXI. Benzene and diphenyl intermediates for 1 : 9-derivatives. H. Gilman and J. R. Thirtle (*J. Amer. Chem. Soc.*, 1944, **66**, 858—859; cf. A., 1944, II, 303).—Metallation of 1 : 2 : 4-$C_6H_3(OMe)_3$ by $LiBu^\alpha$ in boiling Et_2O–N_2 occurs almost exclusively at position 3, since subsequent treatment with I or CO_2 gives 1-*iodo*-2 : 3 : 6-*trimethoxybenzene* (**I**) (51%), m.p. 108—108·5°, or 2 : 3 : 6 : 1-$(OMe)_3C_6H_2{\cdot}CO_2H$ (47%), m.p. 149—150° (lit. 145—146°) (*Me*, m.p. 57—57·5°, and *Et* ester, m.p. 42·5—43°, obtained with difficulty), respectively. Cu powder converts (**I**) at 185—190° and then 210—215° (N_2) into 2 : 3 : 6 : 2′ : 3′ : 6′-*hexamethoxydiphenyl* (76·4%), m.p. 125—125·5°, which with HNO_3–Ac_2O at the b.p. gives the 5 : 5′-$(NO_2)_2$-compound (**II**), m.p. 151—151·5°. HNO_3–AcOH at 60° converts (**I**) into 1-*iodo*-5-*nitro*-2 : 3 : 6-*trimethoxybenzene*, m.p. 119·5—120°, converted by H_2–Pd–$CaCO_3$ in EtOH at 30 lb. into 1 : 3 : 4 : 6-$(OMe)_3C_6H_2{\cdot}NO_2$, m.p. 128—129°, and by Cu powder at 210° and then 230° into (**II**). Attempts to prepare dibenzfuran derivatives are without effect or produce tars. R. S. C.

Vinyl alcohols. IX. Esters of αβ-dimesitylvinyl alcohol. R. C. Fuson, L. J. Armstrong, and W. J. Shenk, jun. (*J. Amer. Chem. Soc.*, 1944, **66**, 964—967).—The alcohol produced by dehydration of hydromesitoin or *iso*hydromesitoin (A., 1943, II, 261) is shown to be *ββ-dimesitylvinyl alcohol* by the prep. of esters of the αβ-dimesityl isomerides and demonstration that these alcohols are too readily ketonised to exist in the free state. CHMesBr·COBr (Mes = mesityl here and below) (prep. from $OH{\cdot}CHMes{\cdot}CO_2H$ by PBr_3 at 100°), b.p. 138—139°/9 mm., with granulated Zn in Et_2O gives a solution of CHMes:CO, which could be isolated only as *dimer*, m.p. 197—200°, but which with MgMesBr–Et_2O and then BzCl gives trans-*αβ-dimesitylvinyl benzoate*, m.p. 147—148°. In NaOH–EtOH–H_2O at the b.p. this undergoes hydrolysis and ketonisation to $COMes{\cdot}CH_2Mes$ (**I**); it shows no active H (Grignard machine) and gives no Cu derivative; its structure is thus proved. With MgMeI, (I) evolves 0·96 CH_4 but then regenerates (**I**); other attempts to prepare its enol also failed. MgEtBr and (**I**) in Et_2O give, after treatment with BzCl or AcCl, cis-*αβ-dimesitylvinyl benzoate*, m.p. 104—105·5° [no active H; hydrolysis gives (**I**)], or *acatate*, m.p. 68—69°, b.p. 188—193°/4 mm., respectively. *Mesitylglyoxalhydrazone*, m.p. 1·9—131°, HgO, $CaSO_4$, and a trace of KOH–EtOH in light petroleum give *mesityldiazomethane*, m.p. 59—61° (decomp.), whence no ketene could be obtained but whence boiling H_2O yields $CH_2Mes{\cdot}CO_2H$. 2 : 4 : 6 : 1-$C_6H_2Et_3{\cdot}CHBr{\cdot}COBr$ (prep. as above), b.p. 140—142°/5 mm., with Zn in Et_2O–Bu_2O gives a keten solution, whence H_2O yields 2 : 4 : 6 : 1-$C_6H_2Et_3{\cdot}CH_2{\cdot}CO_2H$. 2 : 4 : 6 : 1-$C_6H_2Pr^\beta_3{\cdot}COMe$ and SeO_2 give 2 : 4 : 6 : 1-$C_6H_2Pr^\beta_3{\cdot}CO{\cdot}CHO$ (**II**), b.p. 138—143°/7·5 mm., converted by 10% KOH at 100° into 2 : 4 : 6-*triisopropylmandelic acid*, m.p. 163—164° (corr.) (*Me* ester, m.p. 94—95°), which with H_2SO_4–$COMe_2$ at 0° gives the *dioxolone*, m.p. 165—165·5°, and thence (N_2H_4,H_2O–EtOH) the *hydrazide*, m.p. 156—157°. HgO etc. converts the *hydrazone*, m.p. 153—154° (decomp.), of (**II**) into the diazo-compound, decomp. 104° or 125°, whence H_2O yields 2 : 4 : 6 : 1-*triisopropylphenylacetic acid* (**III**), m.p. 146—146·5°. 2 : 4 : 6 : 1-$C_6H_2Pr^\beta_3{\cdot}CH_2Cl$ with CuCN in C_5H_5N at 210—220° gives 2 : 4 : 6-*triisopropylbenzyl cyanide*, m.p. 81—82°, b.p. 129—130°/4 mm., converted by KOH–H_2O–diethylene glycol at the b.p. into (**III**) but by KOH–EtOH into the *amide*, m.p. 170—171°.
R. S. C.

Vinyl alcohols. X. ββ-Diarylvinyl alcohols. R. C. Fuson, P. L. Southwick, and S. P. Rowland (*J. Amer. Chem. Soc.*, 1944, **66**, 1109—1112; cf. supra).—$CMes_2{:}CH{\cdot}OH$ (Mes = mesityl here and below) (**I**), m.p. 129—129·5° (A., 1943, II, 261) [*acetate* (**II**), m.p. 132·5—133°; *benzoate*, m.p. 175·5—176°], is obtained (80%) with a *dimer*, m.p. 189—191°, and a *trimer*, m.p. 290—292°, from hydromesitoin by 55% H_2SO_4 at 100° and from *iso*hydromesitoin (**III**) similarly or, less well, by boiling AcOH–conc. HCl, P_2O_5, or heating at 285°. It is unaffected by O_2 in $COMe_2$. $KMnO_4$ does not affect (**II**) whilst O_3 in CCl_4 gives $CHMes_2{\cdot}CO_2H$; hydrogenation at 200°/3000 lb. yields CH_2Mes_2. Attempts to ketonise (**I**) failed: boiling HCl–MeOH yields the *Me ether* (**IV**), m.p. 129—130°, also obtained from (**III**) by HCl–MeOH at room temp. and converted by HI–AcOH into (CHMes:)$_2$; the *Et ether*, m.p. 96—97°, is obtained from (**I**) by HCl–EtOH. (**I**) is unaffected by Hg–Zn–HCl–AcOH, but with Zn dust at 300° or HI–AcOH at 100° gives $(CHMes:)_2$ and with H_2–Raney Ni–EtOH at 200° gives *ββ-dimesitylethyl alcohol* (**V**), m.p. 118—119° (*acetate*, m.p. 164—165°; *benzoate*, m.p. 151·5—152·5°) (and a little CH_2Mes_2), which is also obtained from (**I**) by H_2–Cu chromite. With CrO_3–AcOH at room temp. (**V**) yields $COMes_2$, with aq. H_2SO_4 at 100° gives $(CHMes:)_2$, and with red P–I–AcOH–H_2O gives $(CH_2Mes)_2$ [also obtained similarly from (**I**)]. O_3 in CCl_4 oxidises (**I**) to mesitoin, CrO_3–AcOH at room temp. or SeO_2 yields mesitil, $KMnO_4$ in aq. $COMe_2$, KOH–EtOH, or NaOCl gives a dimeric *product* (**VI**), $C_{40}H_{46}O_2$, m.p. 184·5—185° (decomp.). (**VI**) contains 1 active H, gives violet to red colours in solution at 70°, is unaffected by H_2–PtO_2 at 1 atm., and with hot HCl–MeOH or –EtOH gives a *compound*, $C_{35}H_{41}O_5$, m.p. 180—181°. CrO_3–AcOH oxidises (**III**) to $MesCO_2H$. With red P–I–AcOH–H_2O, (**III**) gives $(CH_2Mes)_2$, with HI–AcOH at 100° or conc. H_2SO_4 at 0° gives $(CHMes:)_2$, and with PCl_5–$POCl_3$ at room temp. gives *αβ-dichloro-αβ-dimesitylethane*, m.p. 176—179°, also obtained similarly from (**I**) and (? with a diastereoisomeride) from $(CHMes:)_2$ by PCl_5–$CHCl_3$ [crystallisation from MeOH gives also some (**IV**)], and converted by EtOH–KOH into *dimesitylacetylene*, m.p. 127—128·5°. With Cu chromite in EtOH–N_2 at 200°/1500 lb., (**III**) gives MesCHO. iso*Duraldehyde*, m.p. 22—25°, b.p. 112—114°/3 mm., in O_2 gives $ArCO_2H$ and with Mg–MgI_2 gives *hydro*iso*duroin*, m.p. 225·5—226·5° (with some $CAr_2{:}CH_2$), converted by boiling H_2SO_4–AcOH into *ββ-diisodurylvinyl alcohol*, m.p. 149·5—151·5° (*benzoate*, m.p. 156·5—158°), unaffected by air. R. S. C.

Toxic principles of poison ivy. II. Preparation and properties of diphenylmethylene ethers of pyrocatechols.—See A., 1944, II, 346.

Effect of bases on the hydrogenation of alkylphenols in the presence of Raney nickel. H. E. Ungnade and (Miss) D. V. Nightingale (*J. Amer. Chem. Soc.*, 1944, **66**, 1218—1220).—Hydrogenation (Raney Ni) of an alkylphenol is promoted by a small amount of its Na salt, best in absence of solvent (cf. A., 1944, II, 160). Differences in rate of hydrogenation of isomerides are removed by this catalysis, but the ratio of stereoisomeric *cyclo*hexanols formed is unaffected except at high temp. R. S. C.

Semihydrobenzoin and semipinacolic transformations in the α-phenyl-β-methyl- and -ethyl-Δ$^\gamma$-butene-αβ-diol series. Y. Deux (*Compt. rend.*, 1943, **216**, 776—778; cf. A., 1939, II, 265).—$CHPh{:}CMe{\cdot}CH{:}CH_2$ and HgO–I in Et_2O–H_2O give $CHPhI{\cdot}CMe(OH){\cdot}CH{:}CH_2$, which with conc. aq. $AgNO_3$ affords *γ-phenyl-Δ$^\delta$-penten-β-one* (**I**), b.p. 110—111°/14 mm. (*oxime*, m.p. 101—102°; *semicarbazone*, m.p. 138—139°) (semipinacolic change), hydrogenated (Raney Ni) to $CHPhEt{\cdot}COMe$ (*semicarbazone*, m.p. 187—188°). $CHPhCl{\cdot}CMe(OH){\cdot}CH{:}CH_2$, m.p. 84—85°, and MgEtBr give (**I**), also obtained from HNO_2 and $NH_2{\cdot}CHPh{\cdot}CMe(OH){\cdot}CH{:}CH_2$ (*picrate*, m.p. 213—214°) (prepared from the corresponding epoxide and excess of NH_3 at 110—120° in a sealed tube). *α-Phenyl-β-ethyl-Δ$^\gamma$-butene-αβ-diol*, m.p. 93—94° (*di*-p-*nitrobenzoate*, m.p. 107—108°), prepared from the corresponding epoxide and acidulated H_2O at 70—80° for 2 hr., is converted by 30% H_2SO_4 into *α-phenyl-α-ethyl-Δβ-butenaldehyde*, b.p. 116—117°/15 mm. (*semicarbazone*, m.p. 160°; *oxime*, m.p. 98—99°) (semihydrobenzoin change).
$NH_2{\cdot}CHPh{\cdot}CEt(OH){\cdot}CH{:}CH_2$ (*picrate*, m.p. 145—146°) and HNO_2 give $CH_2{:}CH{\cdot}CHPh{\cdot}COEt$ (*loc. cit.*). A. T. P.

Halogenohydrins obtained by the action of hydracids on stilbene oxide. D. Reulos (*Compt. rend.*, 1943, **216**, 774—776).—*trans-αβ-*

Epoxy-αβ-diphenylethane (stilbene oxide) (**I**) and excess of conc. HCl in Et_2O afford, by a Walden inversion, cis-*β-chloro-αβ-diphenylethanol*, m.p. 77° (p-*nitrobenzoate*, m.p. 103—104°), transformed into (**I**) by aq. KOH, and by $SOCl_2$ in $CHCl_3$ into *cis*-$(CHPhCl)_2$. (**I**) and HBr (*d* 1·38) similarly yield *β-bromo-αβ-diphenylethanol*, m.p. 86° (p-*nitrobenzoate*, m.p. 121—122°), convertible into (**I**) by aq. KOH or into $(CHPhBr)_2$, m.p. 237°, by PBr_3; (**I**) and HI give the *β-I*-compound, m.p. 95—96°, readily decomposed with liberation of I. A. T. P.

Dehydration of *cyclo*hexane-1 : 4-diol. Synthesis of 1 : 4-epoxy-*cyclo*hexane. R. C. Olberg, H. Pines, and V. N. Ipatiev (*J. Amer. Chem. Soc.*, 1944, **66**, 1096—1099).—*trans*- (**I**), m.p. 142°, and *cis-cyclo*Hexane-1 : 4-diol (**II**), m.p. 107° (mixed m.p. curve given), are separated by way of the diacetates, m.p. 103° and 33—34°, respectively. Passing (**I**) in MeOH over activated Al_2O_3 at 275° gives Δ^3-*cyclo*hexenol (**III**) 11·4 and 1 : 4-*epoxycyclohexane* (**IV**) (b.p. 120·1°) 73%; (**II**) gives similarly 28 and 27%, respectively, and a 1 : 1 mixture affords 20·6 and 33·5%, respectively. Increasing the temp. reduces the amount of (**IV**), none being formed at 406°. At 350—400° there are obtained also *cyclo*hexadienes, *cyclo*hexene (**V**), methyl*cyclo*hexene, CH_2O, Me_2O, diene polymers, and at 400° a little $CO + H_2$ (from CH_2O). (**V**) is probably formed by hydrogenation of (**IV**) by MeOH to *cyclo*hexanol and subsequent dehydration. In EtOH at 300° only 21·4% of (**IV**) and at 340° none is formed; in $COMe_2$ at 300° 17% of (**IV**) and at 340° none is formed. Boiling the diol over activated Al_2O_3 slowly gives 48·6 mols. of (**IV**) and 18·3 mols. of (**III**). Use of I, $KHSO_4$, H_2SO_4, HBr, or Br gives no (**IV**). Boiling 48% HBr converts (**IV**) into *trans*-1 : 4-dibromo*cyclo*hexane, m.p. 112—113°. R. S. C.

Magnesium dehalogenation of *cis*-chlorohydrins of α-substituted *cyclo*hexanediols; exclusive formation of alkyl*cyclo*hexanones by semipinacolic transformation. M. Tiffeneau, (Mme.) B. Tchoubar, and S. Le Tellier (*Compt. rend.*, 1943, **216**, 856—860; cf. A., 1934, 1098).—2-Chloro*cyclo*hexanone and MgMeI give cis-2-*chloro*-1-*methyl*-cyclo*hexanol* (**I**), b.p. 83—84°/13 mm., purified from some *trans*-compound by removal of the latter as epoxide by aq. KOH. (**I**) and 1 mol. of MgEtBr yield 2-methyl*cyclo*hexanone (semicarbazone, m.p. 189°). Similarly prepared, using MgEtBr or $MgBu^aBr$, are cis-2-*chloro*-1-*ethyl*-, b.p. 96—100°/18 mm., or -1-*butyl*-cyclo*hexanol*, b.p. 96—99°/18 mm., and thence 2-ethyl- (semicarbazone, m.p. 165°) or 2-butyl-*cyclo*hexanone (semicarbazone, m.p. 145°), respectively. 2-*Chloro*-1 : 4-*dimethyl*-, b.p. 92—94°/17 mm., or 2-*chloro*-1 : 5-*dimethyl*-cyclo*hexanol*, b.p. 88—90°/14 mm., afford 2 : 4-dimethyl- (semicarbazone, m.p. 190°) or 2 : 5-dimethyl-*cyclo*hexanone (semicarbazone, m.p. 170°), respectively. Thus the dehalogenation of *cis*-chlorohydrins of *cyclo*hexanediols gives *cyclo*hexanones, whereas the *trans*-isomerides yield *cyclo*pentyl ketones. Mechanisms of reactions are discussed. A. T. P.

Alicyclic sulphur compounds. M. Mousseron (*Compt. rend.*, 1943, **216**, 812—814).—2-Chloro*cyclo*hexanol (**I**) and thiol*cyclo*hexane [Na derivative (**II**)] in hot EtOH give 2-*hydroxydi*cyclo*hexyl sulphide* (**III**), b.p. 170°/12 mm.; similarly prepared are 2-*hydroxydi*cyclo*pentyl sulphide*, b.p. 157°/12 mm., and 2-cyclo*pentylthiol*cyclo*hexanol*, b.p. 165°/12 mm. (**II**) and epoxy*cyclo*hexane (**IV**) give a mixture, b.p. 170°/12 mm., of two stereoisomerides of (**III**). Na_2S_2–EtOH yields *di*-(2-*hydroxy*cyclo*pentyl*) *disulphide*, m.p. 70—71°, and [from (**I**)] *di*-(2-*hydroxy*cyclo*hexyl*) *disulphide* (**V**), m.p. 156—157°; (**IV**) similarly gives stereoisomerides. (**V**) and Sn–HCl afford *di*-(2-*hydroxy*cyclo*hexyl*) *sulphide*, m.p. 71° (*Et*$_1$, b.p. 165°/15 mm., and *Et*$_2$ *ether*, b.p. 190°/15 mm.) (probably through 2-thiol*cyclo*hexanol by loss of H_2S), also obtained from (**IV**) and H_2S or KHS. (**II**) and 2-chloro*cyclo*hexylamine give 2-*aminodi*cyclo*hexyl sulphide*, b.p. 160°/15 mm. [*hydrochloride*, m.p. 200° (decomp.)]; Na_2S_2 yields *di*-(2-*amino*-cyclo*hexyl*) *disulphide*, b.p. 200°/15 mm. [*hydrochloride*, m.p. 230° (decomp.)]. Epithiomethene*cyclo*hexane (liquid) (from Na_2S and 1-thiocyano-1-thiocyanomethyl*cyclo*hexane) is converted by hot H_2O into *di*-(1-*hydroxymethylcyclohexyl*) *sulphide*, m.p. 55°, also obtained from Na_2S and 1-chloro-1-hydroxymethyl*cyclo*hexane (Tiffeneau *et al.*, A., 1937, II, 414). The appropriate Mg 3-methyl-*cyclo*hexyl chloride and SO_2, followed by $KMnO_4$ oxidation of the product, give, through the K salts, $[\alpha]_{546}$ +2·02° in H_2O, and $[\alpha]_{546}$ +1·25° in H_2O, respectively, the cis-, m.p. 95°, $[\alpha]_{546}$ +2·16° in C_6H_6, and trans-3-*methyl*cyclo*hexanesulphonic acid*, m.p. 93°, $[\alpha]_{546}$ +1·44° in C_6H_6. A. T. P.

Condensation of 4-chloro-3 : 5-dinitrobenzaldehyde with malonic acid in presence of organic bases. D. S. Mittal (*J. Indian Chem. Soc.*, 1944, **21**, 34).—C_5H_5N, piperidine, and quinoline (0·15 mol.) successfully catalyse the condensation of equimol. mixtures of 3 : 5 : 4 : 1-$(NO_2)_2C_6H_2Cl$·CHO and $CH_2(CO_2H)_2$. Yields of 84—92% of 4-*chloro*-3 : 5-*dinitrocinnamic acid*, m.p. 82°, are obtained. C. R. H.

Antispasmodics. VI. F. F. Blicke and R. F. Feldkamp (*J. Amer. Chem. Soc.*, 1944, **66**, 1087—1091; cf. A., 1944, II, 14).—1-$C_{10}H_7$·CH_2·CO_2Et (prep. from 1-$C_{10}H_7$·CH_2Cl by KCN and then hot H_2SO_4–EtOH), b.p. 180—181°/15 mm., $Et_2C_2O_4$, and NaOEt in EtOH give an ester, which at 175°/15 mm. yields CO and 1-$C_{10}H_7$·$CH(CO_2Et)_2$ (69%), m.p. 62° (lit. 59—60°). The derived Na compound (prep. in xylene) with RI in boiling C_6H_6 gives 22—75·6% of pure *Et*$_2$ 1-*naphthyl-methyl*-, m.p. 46—47°, b.p. 170—171°/2—3 mm., *-ethyl*-, m.p. 48—49°, b.p. 171—174°/3 mm., -n-*propyl*-, m.p. 51—52°, b.p. 182—184°/4 mm., and -n-*butyl-malonate*, 1-$C_{10}H_7$·$CR(CO_2Et)_2$, m.p. 53—54°, b.p. 185—188°/4 mm., hydrolysed by boiling KOH–EtOH–H_2O to the malonic acids, which at 180° yield α-1-naphthyl-propionic, m.p. 148—149° (lit. 148°), -n-*butyric*, m.p. 86—87°, -n-*valeric* (**I**), b.p. 190°/4 mm., and -n-*hexoic acid* (**II**), m.p. 64—65°, b.p. 183°/3 mm. $C_{10}H_8$, $COCl·CO_2Et$, and $AlCl_3$ in $(CHCl_2)_2$ give 69% of mixed esters, separated by picric acid into 1- (46%), b.p. 167°/3 mm., and 2-$C_{10}H_7$·CO·CO_2Et, b.p. 161—165°/2—3 mm., hydrolysed by Na_2CO_3 in boiling aq. EtOH to the acids, m.p. (**III**) 112—113° and 92—93°, respectively (cf. lit.). MgRBr and (**III**) in Et_2O give 1-$C_{10}H_7$·CPh(OH)·CO_2H, softens ~90°, m.p. (complete) 147°, *α-hydroxy-α-1-naphthyl*-n-*valeric*, m.p. 139—140°, and -n-*hexoic acid*, m.p. 116—117°, reduced by red P and I to 1-$C_{10}H_7$·CHPh·CO_2H, (**I**), and (**II**), respectively. The basic alkyl chloride and CHArR·CO_2H in boiling $Pr^\beta OH$ give: *β-diethylaminoethyl α-1-naphthyl-acetate hydrochloride*, m.p. 128—130°, *-propionate hydrochloride*, m.p. 98—100°, and -n-*butyrate hydrochloride* (**IV**), m.p. 117—119°, and *α-phenyl-α-1-naphthylacetate hydrochloride*, m.p. 124—126°; the *β-piperidinoethyl* ester *hydrochlorides*, m.p. 122—124°, (**V**) 115—117°, 139—140°, and 167—168°, respectively; the *γ-diethylamino*-n-*propyl* ester *hydrochlorides*, m.p. 110—111°, 90—94°, 97—98°, and (**VI**) ~107°, respectively. The *β-morpholinoethyl* ester *hydrochlorides*, m.p. 131—132°, 148—149°, 167—168°, and ~110°, respectively, are obtained from CHArR·COCl and the basic alcohol in C_6H_6 at 0° and then the b.p. *β*-Piperidinoethyl chloride, b.p. 69°/12 mm., gives a hydrochloride, m.p. 229—230° (lit. 208°, 231°). The esters have antispasmodic action at 1 : $\ll 10^5$ to 1 : $\ll 2 \times 10^6$, the morpholino-esters being least, and (**IV**)—(**VI**) being most, effective. R. S. C.

Nitro-amino-derivatives of *o*-bromobenzoic acid. H. Goldstein and G. Preitner (*Helv. Chim. Acta*, 1944, **27**, 888—891).—Gradual addition of 5 : 2 : 1-NHAc·$C_6H_3Br·CO_2H$ to HNO_3 (*d* 1·5) gives 2-*bromo*-6-*nitro*-*o*-*acetamidobenzoic acid*, m.p. ~250° (decomp.), also obtained by oxidising 6 : 1 : 2 : 5-$NO_2·C_6H_2MeBr·NHAc$ (**I**) with aq. $KMnO_4 + MgSO_4$. It is hydrolysed by boiling 10% KOH to 2-*bromo*-6-*nitro*-5-*aminobenzoic acid*, m.p. 218°. Nitration of 1 : 2 : 5-$C_6H_2MeBr·NHAc$ gives mainly 4 : 1 : 2 : 5-$NO_2·C_6H_2MeBr·NHAc$ (**II**) with some (**I**) and 2-*bromo*-4 : 6-*dinitro*-5-*acetamidotoluene*, m.p. 224—225° (cf. Cohen *et al.*, *J.C.S.*, 1914, **105**, 513). (**II**) is oxidised to 2-*bromo*-4-*nitro*-5-*acetamido*-, m.p. 208°, hydrolysed to 2-*bromo*-4-*nitro*-5-*amino*-, m.p. 236·5°, -*benzoic acid*. M.p. are corr. H. W.

Synthesis of alkyl and dialkylaminoalkyl esters of 5-fluoro-2-nitro- and -2-amino-benzoic acid. L. S. Fosdick and R. Q. Blackwell (*J. Amer. Chem. Soc.*, 1944, **66**, 1165—1166).—5-*Fluoro*-2-*nitrobenzoyl chloride* (prep. from the acid by $SOCl_2$), b.p. 130—140°/6—7 mm., yields, by the usual methods, *Me*, m.p. 36·5—37°, *Et*, m.p. 43·5—44°, Pr^a, b.p. 127—128°/3 mm., Bu^a, b.p. 152°/7 mm., $NR_2·[CH_2]_2$ [R = Me (*hydrochloride*, m.p. 154—155°), Et (*hydrochloride*, m.p. 147·5—148·3°), Pr^a (*hydrochloride*, m.p. 131—131·5°), and Bu^a (*hydrochloride*, m.p. 74·5—75·5°)], and $NR_2·[CH_2]_3$ [R = Et (*hydrochloride*, m.p. 137·5—138·2°), Pr^a (*hydrochloride*, m.p. 122—122·5°), and Bu^a (*hydrochloride*, m.p. 98·3—99·3°)] *o-fluoro*-2-*nitrobenzoate*, reduced (PtO_2) to *Me*, b.p. 105°/2 mm., *Et*, b.p. 110°/2 mm., Pr^a, b.p. 116°/2 mm., Bu^a, b.p. 130°/2 mm., $NR_2·[CH_2]_2$ [R = Me (*hydrochloride*, m.p. 175°), Et (*hydrochloride*, m.p. 125°), Pr^a (*hydrochloride*, m.p. 165°), and Bu^a (*hydrochloride*, m.p. 125°)], and $NR_2·[CH_2]_3$ [R = Et (*hydrochloride*, m.p. 133—134°), Pr^a (*hydrochloride*, m.p. 145°), and Bu^a (*hydrochloride*, m.p. 107—108°)] 5-*fluoro*-2-*aminobenzoate*, respectively. The aminoalkyl NH_2-esters produce anæsthesia of long duration but are irritant and toxic. R. S. C.

Action of trimethylgallazide on cresols. R. O. Pepe (*Anal. Asoc. Quím. Argentina*, 1941, **29**, 124—128).—*o-*, *m-*, and *p*-Cresol in NaOH with 3 : 4 : 5 : 1-$(OMe)_3C_6H_2·CON_3$ in $COMe_2$ yield o-, m.p. 102°, m-, m.p. 124°, and p-*tolyl* 3 : 4 : 5-*trimethylgallate*, m.p. 89°.

Action of trimethylgallazide on monomethyl ethers of diphenols. R. O. Pepe (*Anal. Asoc. Quím. Argentina*, 1942, **30**, 235—239).—3 : 4 : 5 : 1-$(OMe)_3C_6H_2·CON_3$ in $COMe_2$ with *o-*, *m-*, and *p*-OMe·C_6H_4·OH in NaOH yields o-, m.p. 115°, m-, m.p. 102°, and p-*anisyl* 3 : 4 : 5-*trimethoxygallate*, m.p. 89°. F. R. G.

5 : 8-Dichloro-2-naphthoic acid and -2-naphthylamine. H. Goldstein and P. Viaud (*Helv. Chim. Acta*, 1944, **27**, 883—888).—2-$C_{10}H_7·CN$ and Cl_2 in glacial AcOH–I (trace) at 110—120° in bright light give 5 : 8 : 2-$C_{10}H_5Cl_2·CN$, hydrolysed by AcOH–H_2SO_4–H_2O to 5 : 8 : 2-$C_{10}H_5Cl_2·CO_2H$, m.p. 301°. This is converted by MeOH–H_2SO_4 into the *Me* ester (**I**), m.p. 145·5°, and by $SOCl_2$ or PCl_5 into the *chloride*, m.p. 102°, which yields the amide, m.p. 224°, and *anilide*, m.p. 226°. (**I**) and boiling N_2H_4,H_2O afford 5 : 8-*dichloro*-2-*naphthoylhydrazine* (**II**), m.p. 212°, which yields *hydrazones* with $COMe_2$, m.p. 192°, PhCHO, m.p. 239°, *p*-$NO_2·C_6H_4$·CHO, m.p. 284°, and COPhMe, m.p. 204°. (**II**) is transformed by I in boiling EtOH into NN′-*di*-5 : 8-*dichloro*-2-*naphthoylhydrazine*, m.p. 342°. $NaNO_2$ and

H_2SO_4 convert (**II**) into the azide (**III**), m.p. ~108° (decomp.), which with the requisite boiling alcohol affords *Me*, m.p. 161°, and *Et*, m.p. 141°, N-5 : 8-*dichloro*-2-*naphthylcarbamate*. Boiling glacial AcOH converts (**III**) into NN′-*di*-5 : 8-*dichloro*-2-*naphthylcarbamide*, m.p. ~327°. (**III**) and boiling Ac_2O afford (after hydrolysis) 5 : 8 : 2-$C_{10}H_5Cl_2{\cdot}NH_2$ (*Bz* derivative, m.p. 203°), also obtained by chlorinating (β-$C_{10}H_7{\cdot}NH_2)_2,H_2SO_4$ in 80% H_2SO_4 and converted by diazotisation followed by treatment with boiling dil. H_2SO_4 into 5 : 8-*dichloro*-2-*naphthol*, m.p. 143° (*Me ether*, m.p. 74°). 5 : 8-*Dibromo*-2-*naphthol*, m.p. 147° (*Me ether*, m.p. 83°), is derived from 5 : 8 : 2-$C_{10}H_5Br_2{\cdot}NH_2$. M.p. are corr. H. W.

Sulphocarboxylic acids. III. Acid amide-like autocondensation of 3-amino-5-sulphobenzoic acid. P. Ruggli and H. Dahn (*Helv. Chim. Acta*, 1944, **27**, 867—882; cf. A., 1942, II, 197).—The prep. of H_2O-sol. org. compounds of approx. polymeric-homologous character and almost const. solubility in H_2O is described. The corresponding azo-dyes are very similarly adsorbed by Al_2O_3. The NH_2-acids and their dyes are not substantive to cotton in dil. Na_2CO_3; adsorption is not pronounced and the data cannot readily be reproduced. At any rate no such differences are found as might be expected from the great difference in mol. wt. This is possibly due to the very similar solubility. 3 : 5 : 1-$NO_2{\cdot}C_6H_3(SO_3H){\cdot}CO_2H$ gives a *Sr* H_2 salt ($+2H_2O$), *dipyridinium* salt, loses C_5H_5N at ~160° leaving the pyridinium H salt, m.p. 202—203°, and a *di*(*benzylthiuronium*) salt, m.p. 173—174°. The presence of 3 : 5 : 1-$NO_2{\cdot}C_6H_3(SO_2Cl){\cdot}COCl$ in 3 : 5 : 1-$NO_2{\cdot}C_6H_3(SO_2Cl){\cdot}CO_2H$ (**I**) (cf. Shah *et al.*, A., 1933, 1293) is determined by the formation of the alkali-insol. dianilide under the action of NH_2Ph. 3 : 5 : 1-$NH_2{\cdot}C_6H_3(SO_3H){\cdot}CO_2H$ is readily obtained by catalytic reduction (H_2 at 80°/50 atm.–Raney Ni in neutral solution) of the NO_2-compound. The normal Sr salt ($+2H_2O$), sol. in 8·3 parts of H_2O at 20°, *monopyridinium*, softens greatly with evolution of C_5H_5N at 176—178°, and non-cryst. benzylthiuronium salt are described. The acid and Sr salt give a blue, the pyridinium a yellow, fluorescence in ultra-violet light. Neutralisation of an aq. suspension of 3 : 5 : 1-$NH_2{\cdot}C_6H_3(SO_3H){\cdot}CO_2H$ at 70—80° with powdered $Sr(OH)_2$ and subsequent alternate additions of (**I**) and $Sr(OH)_2$ give the *Sr* ($+8H_2O$ and $+3H_2O$) salt of 3-3′-nitro-5′-carboxybenzenesulphonamido-5-sulphobenzoic acid; the acid and benzylthiuronium salt are non-cryst. Reduction [$FeSO_4$ and $Sr(OH)_2$] of the NO_2-acid affords the 3′-NH_2-acid, softens at 120—130°, chars at >300° [*Sr* salt (also *hexahydrate*)], and thence by diazotisation the corresponding N_2-acid, very sparingly sol. in hot H_2O. The conversion of (**I**) into 3 : 5 : 1-$NO_2{\cdot}C_6H_3(SO_3H,C_5H_5N){\cdot}CO{\cdot}C_5H_5NCl$ is described. Treatment of (**I**) with C_5H_5N followed by 3 : 5 : 1-$NH_2{\cdot}C_6H_3(SO_3H){\cdot}CO_2H$ leads to 3-3′-nitro-5′-sulphobenzamido-5-sulphobenzoic acid [*tri*(*benzylthiuronium*) salt, m.p. 180°], which is relatively stable to hydrolysis. It is reduced by $FeSO_4$ and $Sr(OH)_2$ or catalytically (Raney Ni) to the 3′-NH_2-compound (**II**), chars at >320°, the purity of which is best controlled by potentiometric titration of ·NH_2 with $NaNO_2$. This gives an internal *diazonium* salt, chars at ~320°, which couples with β-$C_{10}H_7{\cdot}OH$ to an azo-dye, m.p. 237—238°. (**II**) and (**I**) give 3-(3′-3″-nitro-5″-sulphobenzamido-5′-sulphobenzamido)-5-sulphobenzoic acid [*tetra*(*benzylthiuronium*) salt, m.p. 179°], reduced to the 3″-NH_2-acid, chars at >300° (Sr salt), which is converted into the diazo-compound, decomp. ~170°, m.p. 210°; this couples with β-$C_{10}H_7{\cdot}OH$ in C_5H_5N to a dye, m.p. 235—236°. H. W.

Condensation of 2-acetylnaphthalene with diethyl succinate. W. S. Johnson and A. Goldman (*J. Amer. Chem. Soc.*, 1944, **66**, 1030—1037).—Contrary to Stobbe *et al.* (A., 1911, i, 374), 2-$C_{10}H_7Ac$ and $(CH_2{\cdot}CO_2Et)_2$ with NaOEt in Et_2O give 18% of β-carbethoxy-γ-2-naphthyl-*cis*-Δ^β-pentenoic acid (**I**) (*A*) (R = Et, R′ = H), m.p. 119—119·5° (119—119·6°), but with NaOEt (~1 mol.) in boiling

$CO_2R{\cdot}C{\cdot}CH_2{\cdot}CO_2R'$	$CO_2R'{\cdot}CH_2{\cdot}C{\cdot}CO_2R$
2-$C_{10}H_7{\cdot}C{\cdot}Me$	2-$C_{10}H_7{\cdot}C{\cdot}Me$
(*A*.)	(*B*.)

EtOH give 21% of cryst. (**I**) and an oil, which by treatment with $Ba(OH)_2$ and then AcCl gives the *anhydride* (**II**), m.p. 155·5—156°, of β-*carboxy*-γ-2-*naphthyl*-cis-Δ^β-*pentenoic acid* (**III**) (*A*) (R = R′ = H) (see below) with larger amounts of the *anhydride* (**IV**), m.p. 116—116·5°, of the trans-*dicarboxylic acid* (**V**) (*B*) (R = R′ = H) (see below). Structures are proved as follows. In boiling $Ba(OH)_2$–H_2O–EtOH, (**I**) gives (**III**), m.p. 179·5—180·5° (decomp.) [a further impure crop, m.p. 163—165° (decomp.), could not be purified; cf. Stobbe *et al.* (*loc. cit.*)], whence AcCl at room temp. yields (**II**), boiling EtOH containing a drop of H_2SO_4 converts (**II**) into *Et* β-*carboxy*-γ-2-*naphthyl*-cis-Δ^β-*pentenoate* (**VI**) (*A*) (R = H, R′ = Et), *forms*, m.p. 118·5—119° and 105—105·5°, which is also obtained by partially esterifying (**III**) in EtOH–C_6H_6 + a little H_2SO_4 with continuous removal of H_2O. Such treatment with EtOH–C_6H_6–H_2SO_4 converts (**I**) into the cis-*Et*$_2$ ester (*A*) (R = R′ = Et), b.p. 184—186°/0·05—1 mm., which is also obtained from (**VI**) by boiling and is reconverted into (**I**) by partial hydrolysis by $(NH)_2$–EtOH–H_2O. Hydrolysis of (**IV**) by 2% NaOH yields (**V**), m.p. 167—168° (decomp.), reconverted into (**IV**) by AcCl. EtOH + a little H_2SO_4 converts (**IV**) into *Et* β-*carboxy*-γ-2-*naphthyl*-trans-Δ^β-*pentenoate* (**VII**) (*B*) (R = H, R′ = Et), m.p. 102—102·5°, whence hydrolysis and then dehydration regenerates (**IV**) and H_2SO_4–EtOH–C_6H_6 (as above) yields the oily trans-*Et*$_2$ ester, converted by partial hydrolysis into β-*carbethoxy*-γ-2-*naphthyl*-trans-Δ^β-*pentenoic acid* (**VIII**) (*B*) (R = Et, R′ = H), an oil (derived *anilide-acid*, m.p. 153—154°). With O_3 in EtOAc and then Raney Ni at room temp. and finally the b.p., (**I**), (**VI**), or (**VII**) yields 39—42% of 2-$C_{10}H_7Ac$. With a little NaOAc in boiling AcOH–Ac_2O, (**VI**) gives *Et* 3-*methyl*-6 : 7-*benz*-1-*indone*-2-*acetate* (**IX**), m.p. 96·5—97°, and (**II**). With HNO_3 at 190—200° (**IX**) gives 1 : 2 : 3 : 4-$C_6H_2(CO_2H)_4$, with boiling conc. HCl gives the *lactone* (**X**), m.p. 168·5—169° [with $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$ gives a *compound*, $C_{17}H_{17}O_4N_3$, m.p. 244° (decomp.) (bath preheated at 239°)], of 3-*hydroxy*-3-*methyl*-6 : 7-*benz*-1-*hydrindone*-2-*acetic acid* (**XI**) (see below), and with H_2–30% Pd–C in EtOAc gives *Et* 3-*methyl*-6 : 7-*benz*-1-*hydrindone*-2-*acetate*, m.p. 70·2—70·6°. 5% NaOH at room temp. hydrolyses (**X**) to (**XI**), m.p. 169—169·5° (decomp.) [a *form*, m.p. 148·5—150° (decomp.), may also exist] [and red, amorphous material, m.p. 227—235° (decomp.)], which regenerates (**X**) in presence of traces of acid. (**I**) is largely unchanged by NaOAc–AcOH–Ac_2O, giving only a trace of (**II**), but with HF yields (**X**). NaOAc–AcOH–Ac_2O cyclises (**VIII**) to *Et* 4-*acetoxy*-1-*methylphenanthrene*-2-*carboxylate* (**XII**) (78%), m.p. 127·5—128°, hydrolysed by boiling HCl–EtOH to the 4-*OH*-ester (**XIII**), m.p. 178·5—179°, whence Me_2SO_4–aq. NaOH yields *Et* 4-*methoxy*-1-*methylphenanthrene*-1-*carboxylate*, m.p. 74—74·5°, and thence the 4-*OMe-acid*, m.p. 225—225·5°, which with Cu powder in quinoline at 205°, rising to 220°, gives 4-methoxy-1-methylphenanthrene, m.p. 78—79° [picrate, m.p. 183—184° (lit. 182—183°)]. 5% KOH–EtOH hydrolyses (**XII**) to 4-*hydroxy*-1-*methylphenanthrene*-2-*carboxylic acid* (**XIV**), m.p. 253—254° (decomp.; uncorr.) (*acetate*, m.p. 227·5—229°), which is too sensitive for decarboxylation. (**VII**) is not cyclised by NaOAc–Ac_2O–AcOH, yielding only a little (**IV**). HF cyclises (**III**) to 3-*methyl*-6 : 7-*benz*-1-*indone*-2-*acetic acid*, m.p. 215·5—219·5° [could not be obtained from (**IX**)], and some (**X**), and (**V**) gives (**XIV**). The crude product of the original condensation, after separation of much (**I**), is cyclised by NaOAc, whereby (**VIII**) yields (**XII**) and the remaining (**I**) can be isolated; it is thus shown to contain 29% of (**I**) and 30% of (**VIII**); full esterification (to diesters, b.p. 203—206°/2—3 mm.), partial hydrolysis, and then cyclisation indicates 47% of (**I**) and 38% of (**VIII**). Unless otherwise stated, m.p. are corr. R. S. C.

Vitamin-*A* aldehyde (axerophthal). E. G. E. Hawkins and R. F. Hunter (*J.C.S.*, 1944, 411).—Vitamin-*A* aldehyde (**I**), max. at 6570 A. ($SbCl_3$), bands at 3680 and 3500 A. (2 : 4-*dinitrophenylhydrazone*, m.p. 208—209°, prepared in aq. EtOH–HCl–H_2 at 60°; band at 4350 A.), is prepared from vitamin-*A* alcohol (**II**), $Al(OPr^\beta)_3$, MeCHO, and C_6H_6 at 70° for 48 hr. in a sealed tube. Purification is effected by " cyclisation " of unchanged (**II**) and chromatography. Ponndorff reduction with $Al(OPr^\beta)_3$ converts (**I**) into (**II**). In solution, (**I**) is oxidised rapidly at 0° to yield (chromatographic separation) a product which shows bands at 3300 A. and 6180—6200 A. ($SbCl_3$); it differs from (**II**) in that the ultra-violet absorption spectrum is unaltered after treatment with HCl–EtOH. Adding NaOEt–EtOH to (**I**) in $COMe_2$ at −5°, and keeping at room temp. for 2½ hr., gives axerophthylideneacetone, reduced by $Al(OPr^\beta)_3$ to axerophthylidene*iso*propyl alcohol. A. T. P.

Reaction of α-chloroketones with alkali. W. D. McPhee and E. Klingsberg (*J. Amer. Chem. Soc.*, 1944, **66**, 1132—1136).—$COMe{\cdot}CH_2Ph$, b.p. 105—106°/23 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 155·5—156·5°), with SO_2Cl_2–CCl_4 at 45° gives $COMe{\cdot}CHPhCl$ (**I**) (84%), b.p. 115—118°/16 mm., which with $PhSO_2Na$ in boiling 95% EtOH gives α-*benzenesulphonylbenzyl Me ketone* (88%), m.p. 120·5—122·5°. With NaOMe in boiling MeOH, (**I**) gives $Ph{\cdot}[CH_2]_2{\cdot}CO_2Me$ (**II**) (60%), α-*hydroxybenzyl Me ketone Me*$_2$ *acetal* (**III**) (14%), m.p. 63—65°, and $Ph{\cdot}[CH_2]_2{\cdot}CO_2H$ (**IV**) (9%) (cf. Richard, A., 1934, 191; 1935, 979; Aston *et al.*, A., 1942, II, 247), but in MeOH containing a little H_2O gives 48% of (**IV**) and 20% of (**III**). With 2 : 4 : 1-$(NO_2)_2C_6H_3{\cdot}NH{\cdot}NH_2$ (**V**) or $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$, (**III**) gives the bis-derivatives of BzCOMe. $CH_2Ph{\cdot}COCl$ with CH_2N_2 (2 mols.) in Et_2O and then gaseous HCl (cf. Bradley *et al.*, A., 1929, 68) gives *benzyl chloromethyl ketone* (83%), b.p. 133—135°/19 mm. (derived *benzenesulphonylmethyl ketone*, m.p. 89·5—90·5), which with NaOMe–MeOH gives readily 80% of (**II**). $Ph{\cdot}[CH_2]_2{\cdot}COCl$ gives similarly $Ph{\cdot}[CH_2]_2{\cdot}CO{\cdot}CH_2Cl$ (85%), m.p. 39—40° (2 : 4-dinitrophenylhydrazone, m.p. 145—146°), which with NaOMe–MeOH and a little H_2O gives a mixture, b.p. 112—116°/2 mm., of $Ph{\cdot}[CH_2]_2{\cdot}CO{\cdot}CH_2{\cdot}OH$ (**VI**) and $Ph{\cdot}[CH_2]_2{\cdot}C(OMe)_2{\cdot}CH_2{\cdot}OH$ (and 8% of $Ph{\cdot}[CH_2]_3{\cdot}CO_2H$), which after boiling in EtOH + a drop of HCl yields (**VI**) (*phenylhydrazone*, m.p. 114·5—115·5°). *Et* α-*chloro*-α-*benzylacetoacetate* (prep. from $CH_2Ph{\cdot}CHAc{\cdot}CO_2Et$ by SO_2Cl_2 at 0°), b.p. 121—125°/1 mm., in boiling H_2SO_4–AcOH–H_2O gives α-*chloro*-β-*phenylethyl Me ketone* (84%), b.p. 97—99°/4 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 138·5—139·5°), which with NaOMe–MeOH + H_2O gives $\beta\beta$-*dimethoxy*-δ-*phenyl*-n-*butan*-γ-*ol* (54%), b.p. 119—121°/6 mm. This is unaffected by (**V**) in the cold (hydrolysed hot) but after treatment

with hot HCl–EtOH yields $CH_2Ph{\cdot}CO{\cdot}COMe$ [phenylosazone, m.p. 169·5—171° (lit. 172—173°)] and, when kept in Et_2O, gives a *lactolide*, $C_{22}H_{28}O_4$, m.p. 180—182·5°. *S-Benzylthiuronium γ-phenyl-n-butyrate*, m.p. 141—141·5°, and *β-phenylisobutyrate*, m.p. 144—144·5°, are also described. The products, b.p. 104°/0·04 mm. and m.p. 40—41°, of Eastham *et al.* (A., 1944, II, 162) are 3 : 4 : 1-$(OMe)_2C_6H_3{\cdot}[CH_2]_2{\cdot}CO_2R$ in which R = Et (lit. b.p. 193°/20 mm.) and Me (lit. m.p. 37°, 38—39°), respectively. M.p. are corr.

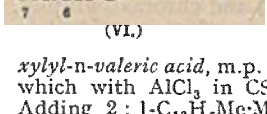
R. S. C.

Reversibility of the benzoin reaction. J. Romo A. (*Ciencia*, 1943, **4**, 216—217).—Benzoin, anisoin, and piperoin in EtOH with $(NH_4)_2CO_3$ and KCN yield the substituted hydantoins obtained by Bucherer *et al.* (A., 1934, 1231) under the same conditions from PhCHO etc. It is concluded that the reaction $2C_6H_4R{\cdot}CHO \rightleftharpoons C_6H_4R{\cdot}CH(OH){\cdot}CO{\cdot}C_6H_4R$ is reversible. Benzil under these conditions yields 5-phenylhydantoin together with EtOBz.

F. R. G.

New aspects of the *ortho*-effect. Cyclic ketones related to acetophenone. R. G. Kadesch (*J. Amer. Chem. Soc.*, 1944, **66**, 1207—1213).—6 : 9-*Dimethylbenzsuberone* (**I**) (see below) behaves towards MgMeI and NH_2OH as a highly hindered ketone [cf. acetomesitylene (**II**)] in contrast to 4 : 7-dimethyl-1-indanone (**III**) and 1-keto-5 : 8-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene (**IV**). This is due to the CO of (**I**) being forced out of co-planarity with the C_6H_6 ring by incorporation into the C_7-ring, so that approach of reagents is blocked by the neighbouring Me, whereas the CO is held co-planar in the C_5- and C_6-rings of (**III**) and (**IV**). This also explains the hindrance exhibited by (**II**), but not by 2 : 4 : 6 : 1-$C_6H_2Me_3{\cdot}CHO$, the CHO being too small. Thus *o*-groups are necessary for hindrance but not alone sufficient. 2 : 1-$C_{10}H_6Me{\cdot}COMe$ (**V**) is hindered, showing that the CH of the adjoining nucleus is sterically effective. (**III**), m.p. 77—78°, is obtained from 2 : 5 : 1-$C_6H_3Me_2{\cdot}CO{\cdot}[CH_2]_2{\cdot}Cl$ by hot conc. H_2SO_4. 3 : 5 : 1-$C_6H_3Me_2{\cdot}CH_2Br$ (prep. from *s*-$C_6H_3Me_3$ by Br in air at 135—155°; 49% yield) and $CHNa(CO_2Et)_2$–EtOH at 60—70° give Et_2 3 : 5-dimethylbenzylmalonate, b.p. 198—205°/24 mm.; the derived *acid*, m.p. 147—148°, at 175—185° yields *β-m-5-xylylpropionic acid*, m.p. 45—46·5°, and thence, by way of the chloride, 5 : 7-*dimethyl-1-indanone*, m.p. 76—77°. 2-*Chloromethyl*-p-*cymene* (prep. from *p*-cymene in 59% yield), b.p. 118—121°/14 mm., yields, as above, Et_2 2-methyl-5-*iso*propylbenzylmalonate, b.p. 186—196°/13 mm., the derived *acid*, m.p. 163°, *β-2-methyl-5-isopropylphenylpropionic acid*, softens 69°, m.p. 83—83·5°, and 4-*methyl*-7-*iso*propyl-1-*indanone*, m.p. 107°.

$CHPh{:}CH{\cdot}CH{:}CH{\cdot}CO_2H$, m.p. 160—164°, yields (H_2–colloidal Pd) $Ph{\cdot}[CH_2]_4{\cdot}CO_2H$, m.p. 56—58°, and thence benz-1-suberone (**VI**), b.p. 141·5—143°/14 mm. 2 : 5 : 1-$C_6H_3Me_2{\cdot}CO{\cdot}[CH_2]_2{\cdot}Cl$ yields, as above, *δ-keto-δ-p-xylyl-n-butane-αα-dicarboxylic acid*, m.p. 117—118° (decomp.) [Et_2 ester, b.p. 215—218° (decomp.)/15 mm.)], *δ-keto-δ-p-xylyl-n-valeric*, m.p. 72—73° (also obtained from *p*-xylene and $COCl{\cdot}[CH_2]_3{\cdot}COCl$), and (Clemmensen) *δ-p-xylyl-n-valeric acid*, m.p. 36·5—37·5°, the chloride (prep. by $SOCl_2$) of which with $AlCl_3$ in CS_2 gives (**I**) (41%), b.p. 121—131°/1 mm. Adding 2 : 1-$C_{10}H_6Me{\cdot}MgBr$ (**VII**) to AcCl gives 2-$C_{10}H_7Me$ and 2 : 1-$C_{10}H_6MeBr$ with only small amounts of (**V**) (reverse addition gives none). 2 : 1-$C_{10}H_6Me{\cdot}CO_2H$ [prep. from (**VII**) by CO_2] with $SOCl_2$ gives the chloride, b.p. 115—120°/1—2 mm., which with MgMeI gives 82% of (**V**), b.p. 122—126°/1 mm. (*ω-CHPh:* derivative, m.p. 136·5—137·5°).



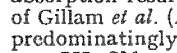
(VI.)

R. S. C.

Action of sodium on ethyl β-methylbutane-αβδ-tricarboxylate. V. R. N. Chakravarti (*J. Indian Chem. Soc.*, 1943, **20**, 399—402; cf. A., 1944, II, 101).—The product (*A*) of the action of Na on Et_3 β-methylbutane-αβδ-tricarboxylate (A., 1943, II, 371) when reduced (Na–Hg) and subsequently esterified gives *Et*$_2$ *3-hydroxy-1-methylcyclopentane-1 : 4-dicarboxylate*, b.p. 145°/5 mm., converted by $POCl_3$ and C_5H_5N, followed by hydrolysis, into 1-*methyl*-Δ^3-*cyclopentene*-1 : 3-*dicarboxylic acid* (**I**), m.p. 168°. None of the isomeric 1-methyl-Δ^2-*cyclo*pentene-1 : 2-dicarboxylic acid was detected, which would be the case if (*A*) contained Et_2 3-methyl*cyclo*pentanone-2 : 3-dicarboxylate (cf. Baker, A., 1931, 957). Reduction (H_2, PtO_2, AcOH) of (**I**) gives a mixture of saturated acids from which *cis*-1-methyl*cyclo*pentane-1 : 3-dicarboxylic anhydride, m.p. 81°, was obtained by action of AcCl. Hydrolysis yielded the *cis*-acid identical with a sample synthesised as follows: dehydration ($POCl_3$–C_5H_5N) of the cyanohydrin of Et 3-methyl*cyclo*pentanone-3-carboxylate followed by hydrolysis gives a mixture (m.p. 155—162°) of unsaturated acids from which *cis*- and *trans*-1-methyl*cyclo*pentane-1 : 3-dicarboxylic acids were obtained on hydrogenation (H_2–PtO_2). (*A*) is therefore Et_2 3-methyl*cyclo*pentanone-3 : 5-dicarboxylate.

J. N. A.

Constituents of pyrethrum flowers. XVI. Heterogeneous nature of pyrethrolone. F. B. LaForge and W. F. Barthel (*J. Org. Chem.*, 1944, **9**, 242—249).—Pyrethrolone (**I**) is a mixture of components differing with respect to the nature of the side-chain. These components can be partly separated by distillation and show marked differences in *n*. Determination of C-Me in successive fractions shows that one component has the conjugated system of double linkings and the other contains a side-chain terminating with the group C:CHMe. The acetate and Me ether are shown to be mixtures corresponding to the two systems of unsaturation. The heterogeneous nature of (**I**) explains the apparent discrepancies between absorption results and chemical facts and revisions of the formulæ of Gillam *et al.* (A., 1942, II, 415) become unnecessary. (**I**) consists predominatingly of the compound



H. W.

Polyenes. II. Purification of β-ionone. W. G. Young, S. J. Cristol, L. J. Andrews, and S. L. Lindenbaum (*J. Amer. Chem. Soc.*, 1944, **66**, 855—857; cf. A., 1944, II, 261).—β-Ionone (**I**) of max. purity (ε 10,700 at 296 mμ.) is obtained from its semicarbazone by cold conc. H_2SO_4 (cf. Heilbron *et al.*, A., 1943, II, 60), but other methods cause partial decomp.; notably distillation in steam with *o*-$C_6H_4(CO)_2O$ gives 80—90%-pure (**I**). (**I**) is not affected by cold conc. or dil. H_2SO_4, and only slowly by hot dil. H_2SO_4.

$CHPh{:}CH{\cdot}CH{:}CH{\cdot}COMe$ and (**I**) react with BzO_2H in C_6H_6 or PhMe at 8° much faster than do Δ^α-mono-unsaturated ketones (*A*) until 1 mol. of BzO_2H is absorbed and thereafter react as slowly as do (*A*); thus the hindrance to addition observed with C:C·CO is not observed with C:C·C:C·CO.

R. S. C.

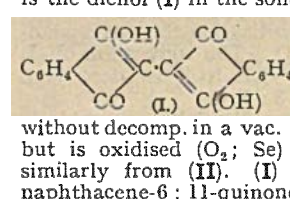
Reported total asymmetric synthesis. J. M. O'Gorman (*J. Amer. Chem. Soc.*, 1944, **66**, 1041).—2-Formyl*cyclo*hexanone with hot MeI–10% EtOH–NaOEt or, better, the Na salt thereof with MeI–PhMe gives 2-formyl-2-methyl*cyclo*hexanone, α 0±0·7° or ±0·1°, respectively.

R. S. C.

Trimeric glyoxal. G. M. Dyson (*Chem. and Ind.*, 1944, 342—343).—Trimeric glyoxal (**I**) may be converted into tetrahydroxy-*p*-benzoquinone by atm. oxidation of its aq. solution in Na_2CO_3, usually in presence of a bisulphite. The benzenoid skeleton must exist in (**I**), which is probably 1 : 1 : 2 : 3 : 4 : 4 : 5 : 6-octahydroxy-Δ^2-*cyclo*hexenone. (Cf. Raudnitz, A., 1944, II, 346.)

F. R. S.

Indene derivatives. III. Constitution and reactions of bishydroxyindone. Photochemical reduction of triketohydrindene. A. Schönberg and R. Moubasher (*J.C.S.*, 1944, 366—367; cf. A., 1943, II, 136).—The violet bis-1 : 3-indanedione (bisdiketohydrindene) (cf. Wanag, A., 1937, II, 199; 1939, II, 326; Eck *et al.*, A., 1935, 1492) is the dienol (**I**) in the solid state and is renamed bishydroxyindone.



It dissolves readily in aq. NaOH and with CH_2N_2–Et_2O gives an orange *Me ether* (**II**), m.p. ~122° (decomp.) (depends on rate of heating), reconverted into (**I**) by conc. H_2SO_4 at 50°. (**I**) sublimes without decomp. in a vac. at 340°. It is stable to O_2 at room temp., but is oxidised (O_2; Se) at 340° to *o*-$C_6H_4(CO)_2O$, also obtained similarly from (**II**). (**I**) is more reactive than 5 : 12-dihydroxynaphthacene-6 : 11-quinone (**III**), although the corresponding resonance structures of (**I**) and (**III**) are similar. (**III**) is only sparingly sol. in aq. NaOH and does not react with CH_2N_2, probably owing to a 6-membered chelate ring (similarly *o*-OH·C_6H_4·COMe does not react with CH_2N_2). The red triketohydrindene is photochemically reduced to the colourless hydrindantin, turns red at ~200° and decomposes at higher temp., by $Pr^\beta OH$ in sunlight for 10 days.

P

IV.—STEROLS AND STEROID SAPOGENINS.

Physico-chemical constants of cholesterol and its ozonide.—See A., 1944, I, 236.

Resinification of cholesterol. A. H. Roffo and L. M. C. Urquiza (*Anal. Asoc. Quím. Argentina*, 1942, **30**, 177—196).—Cholesterol exposed to ultra-violet light from a Cd-vapour lamp is converted into an orange transparent resin, the absorption spectrum and intensity of fluorescence of which have been examined. Resinification is considered as a complex oxidation accompanied by a progressive decrease in m.p., *d*, and I val., and an increase in acidity.

F. R. G.

Marine products. XV. Sterols of starfish. II. W. Bergmann and H. A. Stansbury, jun. (*J. Org. Chem.*, 1944, **9**, 281—289).—The sterol fraction from *Asterias forbesi* is a complex mixture of at least two sterols, the complete separation of which has not been accomplished. Prolonged fractional crystallisation of the sterol mixture (**I**) or of the acetates derived therefrom suggests that the least sol. component is identical with stellasterol (**II**). The discrepancy between the m.p. of the benzoates derived from (**I**) and of stellasteryl benzoate (**III**) depends on isomerisation induced by HCl when (**II**) is heated with BzCl so that (**III**) is a mixture of isomerides such as is also produced when (**II**) is treated with BzCl and C_5H_5N and the product subjected to HCl. Complete separation could not be effected by crystallisation of (**I**), its acetate or benzoate, chromatography of the acetates over Al_2O_3, or bromination of the acetates which destroys most of the material but gives a very small amount of an unknown *dibromide*, $C_{31}H_{50}O_2Br_2$, m.p. 184—185°. Subsequent work is done with (**I**), the degree of unsaturation of which suggests

the presence of di-unsaturated (**II**) and a mono-unsaturated sterol which is termed stellastenol (**IV**). All fractions of starfish sterols and their derivatives are slightly dextrorotatory, indicating the absence of the $\Delta^{5:6}$ double linking; also they all give a green colour reaction with Br usually regarded as typical of sterols with a double linking at $C_{(5)}$. Hence it is assumed as a working hypotheses that (**II**) and (**IV**) have a double linking in the γ- (7 : 8), δ- (8 : 9), or α- (8 : 14) -position. The presence of a double linking in the side-chain of (**II**) is established by ozonolysis, giving *d*-$\alpha\beta$-dimethylbutaldehyde isolated as the 2 : 4-*dinitrophenylhydrazone*, m.p. 119—120°, $[\alpha]_D$ +14·1°. l-$\alpha\beta$-*Dimethylbutaldehyde*-2 : 4-*dinitrophenylhydrazone*, derived from ergosterol, has m.p. 124—124·5°, $[\alpha]_D^{24}$ −37·7°. The mixed m.p. of the two derivatives is 119—122·5°. Bearing in mind that partial racemisation of the aldehydes is difficult to prevent it appears justifiable to conclude that the aldehydes are optical antipodes and that (**II**) has the side-chain $CHMe{\cdot}CH{:}^{24}CHMePr\beta$ in which the optical configuration at $C_{(24)}$ is the opposite of that of ergosterol. Preliminary studies show the presence of inert double linkings in (**I**). Thus a mixture of acetates with 1·4 double linkings absorbed ~0·5 mol. of H_2 with Pt-black catalyst in AcOH at room temp. and atm. pressure, giving a homogeneous α-*stellastenyl acetate*, m.p. 105—106°, $[\alpha]_D^3$ +12·5°, hydrolysed to α-*stellastenol*, m.p. 123—125°, $[\alpha]_D$ +19·8° (3 : 5-*dinitrobenzoate*, m.p. 196·5—197·5°). This is isomerised by HCl in $CHCl_3$ at 0° to β-*stellastenyl acetate*, m.p. 94—96°, $[\alpha]_D$ +19° (hydrolysed to β-*stellastenol*, m.p. 122—124°, $[\alpha]_D^{22}$ +29·5°), which is hydrogenated at room temp. to *stellastanol* (**V**), m.p. 143°, $[\alpha]_D^{22}$ +22° (*acetate*, m.p. 138—139°, $[\alpha]_D^{24}$ +13·5°; 3 : 5-*dinitrobenzoate*, m.p. 204—205°). The optical activites of the two stellastenols and (**V**) agree with the general rule that α-unsaturated sterols have a less positive and β-unsaturated sterols a more positive rotation than the corresponding saturated sterols. (**V**) is isomeric with ergostanol and campestanol and like the latter it differs from ergostanol in the configuration at $C_{(24)}$. The starfish sterols are C_{28} compounds and are the first principal sterols of this order to be found in animal tissue. This complexity is difficult if not impossible to reconcile with the hypothesis of the exogenous origin of the sterols of marine invertebrates. M.p. are corr. $[\alpha]_D$ are in $CHCl_3$. H. W.

Marine products. XVI. 7-Dehydroclionasterol. W. Bergmann, A. M. Lyon, and M. J. McLean (*J. Org. Chem.*, 1944, **9**, 290—292).—Clionasteryl acetate is oxidised by CrO_3 in AcOH at 60—65° to 7-*ketoclionasteryl acetate*, m.p. 172—173°, $[\alpha]_D^{27}$ −99·44°. This is reduced by $Al(OPr\beta)_3$ in $Pr\beta OH$ and then hydrolysed to a mixture of diols; the form of higher m.p. gives a *dibenzoate*, m.p. 159—160°, $[\alpha]_D$ +93·4°, which is transformed by protracted boiling with $NPhMe_2$ into 7-*dehydroclionasteryl benzoate*, m.p. 133—135° (turbid; clear at 138°), also obtained from the dibenzoate of the form of lower m.p. This is hydrolysed by KOH–MeOH to 7-*dehydroclionasterol* (**I**), m.p. 138°, $[\alpha]_D$ −98·2°, which becomes yellow when kept. Better results are obtained by hydrolysing the mixed dibenzoates with NaOMe in MeOH–C_6H_6 and treatment of the product with boiling $NPhMe_2$; (**I**) is then isolated as the digitonide and the latter is converted directly by boiling Ac_2O into 7-*dehydroclionasteryl acetate*, m.p. 139—140°, $[\alpha]_D^{24}$ −71·6°, the absorption spectrum of which is identical with that of ergosteryl acetate. M.p. are corr. $[\alpha]_D$ are in $CHCl_3$. H. W.

Bile acids and related substances. XXX. Simplified preparation of 3(α) : 12(α)-dihydroxyætiocholanic acid. V. Wenner and T. Reichstein (*Helv. Chim. Acta*, 1944, **27**, 965—969).—Me 3(α) : 12(β)-dihydroxyætiocholanate is partly acetylated by boiling Ac_2O–C_6H_6, giving unchanged material, the diacetate, a little of the 12- and (mainly) the amorphous 3-acetate (**I**). Oxidation of (**I**) by CrO_3 in AcOH at 16° yields *Me* 12-*keto*-3(α)-*acetoxyætiocholanate* (**II**), m.p. 152—154°, $[\alpha]_D^{14}$ +151·5°±2° in $CHCl_3$, hydrolysed to the 3(α)-*OH*-ester (**III**), m.p. 169—170°, $[\alpha]_D^{13}$ +144·0°±1° in $CHCl_3$. (**II**) or (**III**) is hydrogenated (Raney Ni in alkaline solution) to Me 3(α) : 12(α)-dihydroxyætiocholanate, m.p. 182—183°, $[\alpha]_D^{14}$ +51·9±2° in MeOH (3-*monoacetate*, m.p. 155—156°, $[\alpha]_D^{16}$ +52·3°±2° in $COMe_2$). M.p. are corr. (block); limit of error ±2°. H. W.

Comparison of methods for the preparation of dehydroandrosterone. S. Schreyer (*Anal. Asoc. Quím. Argentina*, 1941, **29**, 141—148).—The yield of dehydroandrosterone obtained from cholesteryl acetate dibromide by CrO_3 is not related to O consumed. The experimental conditions of Butenandt *et al.* (A., 1936, 77) give a higher yield than those of Ruzicka *et al.* (A., 1935, 1125) or Wallis *et al.* (A., 1935, 1242). F. R. G.

Constituents of the adrenal cortex and related substances. LXIX. Action of lead tetra-acetate on cholestenone. E. Scebeck and T. Reichstein (*Helv. Chim. Acta*, 1944, **27**, 948—950).—The product obtained by oxidising Δ^4-cholesten-3-one with $Pb(OAc)_4$ in AcOH–Ac_2O at 70° (cf. A., 1939, II, 552) is the 2-*OAc*-derivative, m.p. 141—142°, $[\alpha]_D^{15}$ +65·5°±1° in $CHCl_3$, since it is converted by hydrogenation and subsequent hydrolysis into cholestane-2 : 3-diol (possibly a mixture of stereoisomerides) which is oxidised by CrO_3 in AcOH to the homogeneous dicarboxylic acid, m.p. 196—197° (di-Me ester, m.p. 62—64°), also prepared according to Windaus *et al.* (A., 1914, i, 1066) by oxidation of cholestan-3(β)-ol. M.p. are corr. (block); limits of error ±2°. H. W.

Constituents of the adrenal cortex and related substances. LXVIII. Pregnane-3(α) : 11(α)-diol-20-one and -3(β) : 11(α)-diol-20-one. J. von Euw, A. Lardon, and T. Reichstein (*Helv. Chim. Acta*, 1944, **27**, 821—839).—Me 3(β)-11(α)-dihydroxybisnorcholanate is converted when heated with MgPhBr into the amorphous carbinol, the amorphous acetate of which is transformed by boiling AcOH into *αα-diphenyl-β-11(α)-hydroxy-3(β)-acetoxyætiocholanyl-*Δ^{α}*-propene*, m.p. 282—284°. Ozonisation at −10° and fission of the ozonide by Zn dust and AcOH gives $COPh_2$ and a mixture which, after acetylation, is separated chromatographically into *pregnan-3(β)-ol-11 : 20-dione acetate* (**I**), m.p. 169—170°, $[\alpha]_D^{13}$ +89·1°±1·5° in $COMe_2$, and *pregnane-3(β) : 11(α)-diol-20-one* 3-*monoacetate* (**II**), m.p. 163—164°, $[\alpha]_D^{1}$ +115·2°±1·5° in $COMe_2$. Ozonisation at −80° with use of 1 mol. proportion of O_3 and immediate fission of the ozonide leads almost exclusively to (**II**). Alkaline hydrolysis (KOH–MeOH) at 20° of (**I**) and (**II**) gives *pregnan-3(β)-ol-11 : 20-dione* (**III**), m.p. 152—153° (becomes opaque at 100°), and *pregnane-3(β) : 11(α)-diol-20-one* (? hydrate), m.p. 255—260°. (**II**) is readily oxidised by CrO_3 in AcOH to (**I**). By a similar series of changes Me 3(α) : 11(α)-dihydroxybisnorcholanate is transformed into *αα-diphenyl-β-11(α)-hydroxy-3(α)-acetoxyætiocholanyl-*Δ^{α}*-propene*, m.p. 242—245°, and thence into *pregnane-3(α) : 11(α)-diol-20-one* 3-*monoacetate* (**IV**), m.p. 182—184° $[\alpha]_D^{13}$ +147·5°±1·5° in $COMe_2$, hydrolysed to *pregnane-3(α) : 11(α)-diol-20-one*, m.p. 222—225°, and oxidised by CrO_3 in AcOH to *pregnan-3(α)-ol-11 : 20-dione acetate* (**V**), m.p. 132—133°, or, frequently, 138° when heating is slow (in one experiment hexagonal plates, m.p. 134—137°, were observed), $[\alpha]_D^{13}$ +121·7°±3° in $COMe_2$; pregnan-3(α)-ol-11 : 20-dione has m.p. 172—174°.

Pregnan-12(β)-ol-3 : 20-dione is converted by anthraquinone-2-carboxyl chloride and C_5H_5N in C_6H_6 into the *anthraquinone-2-carboxylate*, m.p. 208—209°, which passes at 295—300°/0·05 mm. into Δ^{11}-pregnene-3 : 20-dione, m.p. 131—133°, transformed by NHAcBr and NaOAc,$3H_2O$ in dil. AcOH, into 12-bromopregnan-11(α)-ol-3 : 20-dione, m.p. 245—246° (decomp.) [the by-products afford (on oxidation) Δ^9-pregnene-3 : 12 : 20-trione, m.p. 182—183°]. This is oxidised to 12-*bromopregnane*-3 : 11 : 20-*trione*, m.p. 192—193°, debrominated by Zn dust and NaOAc in AcOH to pregnane-3 : 11 : 20-trione (**VI**), m.p. 161—162°. This when partly hydrogenated (PtO_2 in AcOH) and then pptd. with digitonin and treated with Girard's reagent *T* gives mainly (**III**) characterised as (**II**), also obtained directly by chromatography of the acetylation–hydrogenation product. The by-products of the hydrogenation, if necessary after hydrolysis, are re-converted by cautious oxidation into (**VI**), whereby a good yield of (**III**) is secured. (**III**) (as acetate) is partly hydrogenated to pregnane-3(β) : 20-diol-11-one 3-monoacetate, m.p. 200—201°, identified as the *diacetate*, m.p. 209—210°, and fully hydrogenated to *pregnane*-3(β) : 11(α) : 20-*triol* 3-*monoacetate*, double m.p. ~75° and 166—167°, which is converted by Ac_2O and C_5H_5N at 70° into the 3 : 20-*diacetate*, m.p. 209—210°, by CrO_3 in AcOH into pregnane-3(β) : 20-diol-11-one 3-monoacetate, m.p. 199—200°, and by $Al(OPh)_3$ in C_6H_6–$COMe_2$ at 98° into (**II**).

Pregnane-3(α) : 12(β)-*diol*-20-*one dianthraquinone-2′-carboxylate* (**VII**), m.p. 283—284°, is hydrolysed by $NH_2{\cdot}CH_2{\cdot}CO_2K$ in EtOH–dioxan or KOPh with excess of PhOH in EtOH–dioxan to the 12-*monoanthraquinone-2′-carboxylate* (**VIII**), m.p. 230—231°, which rapidly becomes green on exposure to air and gives an *acetate* (**IX**), m.p. 174—175°. (**VIII**) is oxidised by CrO_3 in AcOH at 18° to pregnan-12(β)-ol-3 : 20-dione anthraquinone-2′-carboxylate, m.p. 209—210°. Pregnane-3(α) : 12(β)-diol-20-one 3-monoacetate, m.p. (indef.) 95—110°, is converted into (**IX**) and a *substance*, m.p. 225—226°. Pregnane-3(α) : 12(β)-diol-20-one and BzCl in C_5H_5N at 20° give the *dibenzoate*, m.p. 183—184°, partly hydrolysed by KOH–MeOH to the 12-*monobenzoate*, m.p. 160—161°, which gives a non-cryst. 3-acetate. At 290°/high vac. (**IX**) gives unchanged material, $\Delta^{3:11}$-*pregnadien-20-one* (**X**), m.p. 125—127°, and Δ^{11}-*pregnen-3(α)-ol-20-one acetate* (**XI**), m.p. 136—137° (hydrolysed to the alcohol, m.p. 125—126°, which is oxidised to Δ^{11}-pregnene-3 : 20-dione, m.p. 132—134°).

Δ^{11}-*Pregnen-3(α)-ol-20-one anthraquinone-2′-carboxylate* (**XII**) has m.p. 240—242°. (**VII**) at 290—320°/0·02 mm. passes into (**X**) with some (**XII**) and (?) Δ^3-*pregnen-12(β)-ol-20-one anthraquinone-2′-carboxylate*, m.p. 190—192°, and some unchanged material. (**XI**), NHAcBr, and NaOAc in dil. AcOH at 16° afford 12-*bromopregnane*-3(α) : 11(α)-*diol*-20-*one* 3-*monoacetate*, m.p. 213—214°, oxidised to 12-*bromopregnan-3(α)-ol-11 : 20-dione acetate*, m.p. 194—195°. This is converted by Zn dust, NaOAc, and AcOH into (**V**). Δ^9-*Pregnen-3(α)-ol-12 : 20-dione acetate*, double m.p. 150—152° and 162—164°, is described. Energetic hydrogenation of (**V**) leads to *pregnane*-3(α) : 11(α) : 20-*triol* 3-*monoacetate*, m.p. 83—85°, converted by $Al(OPh)_3$ in $COMe_2$ into (**IV**). M.p. are corr. (block); limit of error ±2°. H. W.

Introduction of the 3-keto-Δ^4-conjugated system in the deoxycholic acid series. B. Riegel and A. V. McIntosh, jun. (*J. Amer. Chem. Soc.*, 1944, **66**, 1099—1103).—3 : 12-Dihydroxycholic esters are con-

verted by $Al(OBu^{\gamma})_3$ and *cyclo*hexanone in boiling PhMe directly into 12-hydroxy-3-keto-esters. Thus are obtained Me 12-hydroxy-3-keto-cholanate (**I**) (63%), m.p. 140·5—142°, *-norcholanate* (**II**) (65%), m.p. 143—145°, *-bisnorcholanate* (78%), m.p. 203—204°, and -ætiocholanate (37%), m.p. 139—141·5°. With Br–AcOH at room temp. (1·75 min.) these give 4-*Br*-esters, m.p. 134—134·5°, 178·5—180°, 206—207°, and a resin, respectively, which in boiling C_5H_5N yield Me 12-hydroxy-3-keto-Δ^4-cholenate (**III**), m.p. 144—145° (lit. 150—152°), *-Δ^4-norcholenate* (**IV**), m.p. 136·5—137°, *-Δ^4-bisnorcholenate* (**V**), m.p. 164—167° (? 175—176°), and *-Δ^4-ætiocholenate* (**VI**), m.p. 152—153°, respectively. (**III**)—(**VI**) have characteristic absorption max. at 241—241·5 mμ., ε being 14,470, 16,320, 14,100, and 14,940, respectively. Me 3 : 12-diacetoxy-cholanate and *-norcholanate*, m.p. 153—153·4°, in 0·5N-KOH–EtOH at room temp. give 3-hydroxy-12-acetoxy-cholanic and *-norcholanic acid* (82·5%), m.p. 219—221°, oxidised by CrO_3–AcOH to 3-keto-12-acetoxy-cholanic and -norcholanic acid, respectively, and thence, by hydrolysis followed by treatment with MeOH and a little AcCl, (**I**) and (**II**), respectively. *Me* 3 : 12-*diacetoxy-bisnorcholanate*, m.p. 165—167°, and -ætiocholanate, m.p. 149—150·5°, and 12-*hydroxy*-3-*keto*-Δ^4-*bisnorcholenic acid*, m.p. 210—220°, are also prepared. M.p. are corr. R. S. C.

Steroids and sex hormones. XCIX. Synthesis of 12-*epi*-14-deoxy-digoxigenin. L. Ruzicka, P. A. Plattner, and J. Pataki (*Helv. Chim. Acta*, 1944, **27**, 988—994).—3(*a*) : 12(*β*)-*Diacetoxypregnan*-20-*one* (**I**), m.p. 114—115°, $[\alpha]^{17}$ +165·5° in $CHCl_3$, obtained by acetylation of the 3(*a*)-OH-compound, m.p. 208°, $[\alpha]_D^{17}$ +158° in $CHCl_3$, is converted by Zn and $CH_2Br{\cdot}CO_2Et$ followed by hydrolysis into 3(*a*) : 12(*β*) : 20-*trihydroxynorcholanic acid*, m.p. 221—222°, $[\alpha]_D^{1\cdot5}$ +46·4° in EtOH. The *Me* ester, m.p. 158—159°, $[\alpha]^{16\cdot5}$ +33·7° in $CHCl_3$, does not readily lose H_2O when boiled with Ac_2O but is converted into the *triacetate* (**II**), m.p. 162·5—163·5°, $[\alpha]_D^{16\cdot5}$ +70·2° in $CHCl_3$. When sublimed at 170°/high vac., (**II**) gives a non-cryst. material from which after hydrolysis, hydrogenation, and re-acetylation Me diacetylnordeoxycholate is obtained. (**I**) is oxidised by $Pb(OAc)_4$ in AcOH–Ac_2O at 68—72° to 3(*a*) : 12(*β*) : 21-triacetoxypregnan-20-one, m.p. 160·5—151° (lit. 114—115°), $[\alpha]_D^{14\cdot5}$ +156·9° on $CHCl_3$, $[\alpha]_D^{1}$ +153·2° in $COMe_2$, which with Zn and $CH_2Br{\cdot}CO_2Et$ followed by Ac_2O–C_5H_5N gives 12-epi-14-*deoxydigoxigenin* 3 : 12-*diacetate* [$\Delta^{20:22}$-21-*hydroxy*-3(*a*) : 12(*β*)-*diacetoxynorcholenolactone*], m.p. 180—181°, $[\alpha]_D^{15}$ +107·9° in $CHCl_3$, hydrolysed by 2N-HCl in dioxan at 100° to 12-epi-14-*deoxydigoxigenin*, m.p. 253—255°, $[\alpha]_D^{15}$ +51·5° in $CHCl_3$. M.p. are corr. (vac.). H. W.

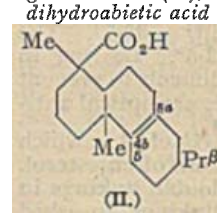
V.—TERPENES AND TRITERPENOID SAPOGENINS.

Terpene series. I. Dehydration of alcohols in the terpene series under pressure and in presence of dilute aqueous salt solutions. V. N. Ipatiev and H. Pines (*J. Amer. Chem. Soc.*, 1944, **66**, 1120—1122).—In aq. $MgCl_2$ at 230°/70 atm. terpineol or *p*-menthane-1 : 8-diol gives *α*-terpinene [liquid tetrabromide, an oil; $(CH{\cdot}CO)_2O$ *adduct*, m.p. 64—65°, and the corresponding *acid*, m.p. 127—128°], dipentene [tetrabromide, m.p. 124—125° (photomicrograph)], and a terpene [*tetrabromide*, m.p. 96° (photomicrograph)]; dehydration occurs without ring-change since hydrogenation and then dehydrogenation (Pt–Al_2O_3) gives *p*-cymene. Similar treatment of dihydroterpineol gives *p*-methyl*iso*propenyl*cyclo*hexane and *dl*-*p*-menthene (**I**), of menthol gives mainly (**I**), and of *iso*borneol gives camphene (**II**) and a small amount of a liquid isomeride (**III**). Borneol is more stable, but in aq. $MgCl_2$ at 285—295° gives (**II**) and an isomeride (**IV**), m.p. −15° (more at higher temp.). HCl converts (**III**) or (**IV**) into *iso*bornyl chloride and hydrogenation gives *iso*bornylene. R. S. C.

Action of selenium dioxide on camphor and α-substituted camphors. J. Vène (*Compt. rend.*, 1943, **216**, 772—774).—Camphor and excess of SeO_2 in boiling EtOH give 27% of camphorquinone (**I**); the yield is 88—90% in PhMe or xylene, and 95% in a little Ac_2O. SeO_2 and *α*-hydroxycamphor give 40% of (**I**) in EtOH (2 hr.), or 85% in absence of solvent (15 min.). *α*-Bromocamphor is almost unattacked by SeO_2 in Ac_2O at 135°, but in absence of solvent at 145—150° (6 hr.) yields 55% of (**I**); *α*-chlorocamphor behaves similarly, giving 30% of (**I**). Ethylcamphor and SeO_2 at 180—190° for 2 hr. yield 12% of (**I**), whereas benzylcamphor is dehydrogenated with SeO_2 at 200° to give 95% of benzylidenecamphor, stable to SeO_2 at 200°. *α*-Oximinocamphor and SeO_2 at 85° (violent reaction) afford 23% of camphor-*α*-mononitrile and 27% of camphoric anhydride; a similar slower reaction occurs in EtOH or PhMe. A. T. P.

Saponins and sapogenins. XXIV. Norechinocystenol-*A* and norechinocystenone-*A*. G. H. Harris and C. R. Noller (*J. Amer. Chem. Soc.*, 1944, **66**, 1005—1006; cf. A., 1944, II, 21).—The CO-ester acetate, in which the CO is *β*- to the CO_2H of echinocystic acid (A., 1939, II, 333), with $N_2H_4{\cdot}H_2O$ and NaOEt–EtOH at 200° gives *norechinocystenol*-A (**I**), m.p. 188—191°, $[\alpha]_D^{5}$ +15·1° in $CHCl_3$ (*acetate*, m.p. 217—220°, $[\alpha]_D^{1}$ +21·6° in $CHCl_3$), the CO being reduced, the Ac removed, and the CO_2H eliminated. CrO_3–AcOH oxidises (**I**) to *norechinocystenone*-A (**II**), m.p. 159—162°, $[\alpha]_D^{21}$ +30·8° in $CHCl_3$. (**I**) differs from oleanol and (**II**) differs from oleanone (cf. A., 1940, II, 311). R. S. C.

Resin acids. Structure of the lactone of hydroxytetrahydroabietic acid. R. F. B. Cox (*J. Amer. Chem. Soc.*, 1944, **66**, 865—870).—The following reactions favour Ruzicka's formula (A., 1941, II, 69) for abietic acid against Fieser's (A., 1938, II, 108) and indicate that lactonisation of hydroxytetrahydroabietic acid occurs at $C_{(4b)}$. With MgMeI in Et_2O–C_6H_6 and then aq. NH_4Cl the lactone (**I**) gives $\Delta^{4b:8a}$- (**II**), m.p. 185—186°, $[\alpha]_D$ −36° in EtOH, and $\Delta^{4b:5}$-*dihydroabietic acid* (**III**), m.p. 147—148°, $[\alpha]_D$ +68° in EtOH. (**II**) and (**III**) are stable in boiling AcOH, but in HCl–EtOH regenerate (**I**); (**III**) lactonises faster than (**II**) does, but unlactonised acid is thereby isomerised to (**II**); (**II**) is not isomerised by this method. (**III**) is hydrogenated (PtO_2; AcOH) faster than is (**II**). With NOCl–AcOH or OBu·NO–HCl, (**II**) gives a blue *8b-NO-lactone*, m.p. 91·5—92°, $[\alpha]_D$ −925° in EtOH, reduced by Na_2S–EtOH–H_2O to the *8b-NH_2-lactone*, m.p. 144—145°, $[\alpha]_D$ +1° in EtOH, and hydrolysed to (**I**) by hot HCl–AcOH. NOCl–AcOH converts (**III**) into the *5-oximino-lactone*, m.p. 184—185°, $[\alpha]_D$ −30° in $CHCl_3$, which with mineral acid undergoes Beckmann rearrangement. R. S. C.



(II.)

VI.—HETEROCYCLIC.

Furfuryl furoate by condensation from furfuraldehyde. E. R. Nielsen (*J. Amer. Chem. Soc.*, 1944, **66**, 1230).—Dissolution of Na (18 g.) in furfuryl alcohol (250 g.) + C_6H_6 (750 c.c.) at the b.p. and gradual addition of distilled furfuraldehyde (1350 g.) gives furfuryl 2-furoate (77·8%), forms, m.p. 18·5° and 27·5°, b.p. 121°/1·5 mm. R. S. C.

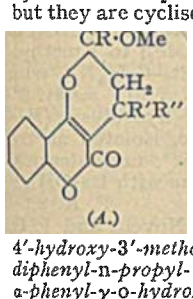
Gossypol. IV. Behaviour of gossypol as an *o*-hydroxy-aldehyde : formation of α-pyrones and flavylium salts. B. Krishnaswamy, K. S. Murty, and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1944, **19, A**, 370—376).—Gossypol (**I**) condenses with $CH_2Ac{\cdot}CO_2Et$ to form a *pyrone*, $C_{38}H_{34}O_{10}$, m.p. >330°, with $CH_2(CO_2Et)_2$ to a *pyrone*, $C_{34}H_{28}O_8(CO_2Et)_2$, m.p. 248—250°, with COPhMe (HCl) to a flavylium *salt*, $C_{46}H_{40}O_8Cl_2$, m.p. 295—297°, and with *ω* : 4-dihydroxy-acetophenone (+HCl) to a flavylium *salt*, $C_{46}H_{40}O_8Cl_2$ (+$3H_2O$), m.p. >320°. These reactions indicate the presence of 2 *o*-OH–CHO groups in (**I**). The dianilino-compound of (**I**) also undergoes the reactions smoothly, indicating that it is easily split up into (**I**) and NH_2Ph under the reaction conditions. F. R. S.

Synthesis of coumarins from *o*-hydroxyaryl alkyl ketones. V. Formation of coumarins from *o*-hydroxyphenyl benzyl ketones. D. Chakravarti and B. C. Bera (*J. Indian Chem. Soc.*, 1944, **21**, 44—46).—5-Methyl-, 5-chloro-, and 3-chloro-2-methoxy-5-methyl-phenyl benzyl ketones condense (Reformatsky) with $CH_2Br{\cdot}CO_2Et$ and $CHMeBr{\cdot}CO_2Et$ to give OH-esters, which on dehydration ($SOCl_2$–C_5H_5N) and demethylation (HI) yield coumarins. The following are described : *Et* 2-*methoxy*-5-*methyl*-*β*-*benzylcinnamate*, b.p. 200—205°/3 mm.; 4-*benzyl*-6-*methylcoumarin*, m.p. 148°; 2-*ethoxy*-5-*methylphenyl benzyl ketone*, b.p. 200—201°/5 mm.; *Et* 2-*ethoxy*-5-*methyl*-*β*-*benzylcinnamate*, b.p. 210—215°/5 mm.; *Et* 2-*methoxy*-*α*-*β*-*benzyl*-*α* : 5-*dimethylcinnamate*, b.p. 203°/2·5 mm.; 4-*benzyl*-3 : 6-*dimethylcoumarin*, m.p. 136°; *Et* 5-*chloro*-2-*methoxy*-*β*-*benzyl*-, b.p. 208°/4 mm., and 5-*chloro*-2-*methoxy*-*β*-*benzyl*-*α*-*methyl*-*cinnamate*, b.p. 212°/2 mm.; 6-*chloro*-4-*benzylcoumarin*, m.p. 101°, and its 3-*Me* derivative, m.p. 162°; 3-*chloro*-2-*hydroxy*-5-*methylphenyl benzyl ketone*, m.p. 110° (2-*OMe*-compound, b.p. 195—200°/3·5 mm.); *Et* 3-*chloro*-2-*methoxy*-5-*methyl*-*β*-*benzylcinnamate*, b.p. 210—215°/4·5 mm. (*α* : 5-*Me*, derivative, b.p. 210°/2 mm.); and 8-*chloro*-4-*benzyl*-6-*methylcoumarin*, m.p. 161° (3 : 6-Me_2 derivative, m.p. 173°). S

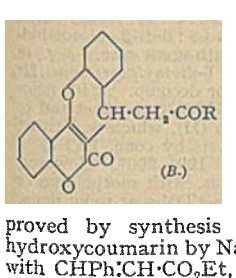
4-Hydroxycoumarins. IV. Esters of 4-hydroxycoumarins. M. A. Stahmann, L. H. Graf, C. F. Huebner, S. Roseman, and K. P. Link. **V. Condensation of αβ-unsaturated ketones with 4-hydroxycoumarin.** M. Ikawa, M. A. Stahmann, and K. P. Link. **VI. Glucosides of 4-hydroxycoumarins.** C. F. Huebner, S. A. Karjala, W. R. Sullivan, and K. P. Link (*J. Amer. Chem. Soc.*, 1944, **66**, 900—902, 902—906, 906—909; cf. A., 1944, II, 166).—IV. 3 : 3′-Alkylidenebis-4-hydroxycoumarins with RCOCl in C_5H_5N at 0° and then 25° give 3 : 3′-methylenebis-4-hydroxycoumarin diacetate (**I**), *dipropionate* (**II**), m.p. 247—248°, *di*-n-, m.p. 227—228°, and -iso-*butyrate*, m.p. 233—234°, *di*-n-, m.p. 224—225°, and -iso-*valerate*, m.p. 220—221°, *di*-n-*hexoate*, m.p. 225—226°, *di*-n-*heptoate*, m.p. 215—216°, *dibenzoate* (**III**), m.p. 263—264°, *di*-*αα*-*dimethylpropionate*, m.p. 210—211°, *di*(*benzylcarbonate*), m.p. 188—189°, *di*(*acetylsalicylate*), m.p. 253—256°, *di*(*carbomethoxysalicylate*) (**IV**), m.p. 213—216°, *di*-(*o*-*benzyloxybenzoate*) (**V**), m.p. 212—213°, *di*-*o*-, m.p. 250—252°, and -*p*-*chlorobenzoate*, m.p. 288—291°, and *di*-2-*furoate*, m.p. 298—300°, 3 : 3′-*ethylidene*-, m.p. 209—210°, 3 : 3-*propylidene*-, m.p. 203—204°, and 3 : 3′-*butylidene*-*bis*-4-*hydroxycoumarin dibenzoate*, m.p. 226—227°, 3 : 3′-*propylidene*-, m.p. 202—203°, and 3 : 3′-*butylidene*-*bis*-4-*hydroxycoumarin diacetate* (**VI**),

m.p. 210—211°. 4-*Acetylsalicyloxy-*, m.p. 183—185°, and 4-*o-benzyloxybenzoyloxy-* (**VII**), m.p. 173—175°, -3-*phenylcoumarin* are similarly obtained. 3 : 3′-Methylene- (**VIII**), -propylidene-, and -butylidene-bis-4-hydroxycoumarin are also diacetylated by boiling Ac_2O alone, but the 3 : 3′-benzylidene- and -ethylidene-coumarins are thus dehydrated to the 4 : 4′-epoxy-compounds. The CHPh:compound is dehydrated also by BzCl–C_5H_5N. Aq. NaOH hydrolyses (**I**) or (**II**) to the parent OH-compound; 1 mol. of NaOEt in boiling EtOH converts (**I**), (**II**), or (**VI**) into the epoxy-compounds and EtOAcyl, probably by way of the monoester since this is also converted into the epoxy-compound by 1 mol. of NaOEt. Boiling aq. NaOAc converts (**IV**) into the epoxy-compound (63%), (**VIII**) (35%), o-OH·C_6H_4·CO_2H, and traces of *o*-CO_2Me·O·C_6H_4·CO_2H. 2 mols. of NaOEt in boiling EtOH convert (**III**) into (**VIII**) and some epoxy-compound. Hydrogenation (Raney Ni; 100°/1900 lb.; dioxan) of (**V**) gives 3 : 3′-*methylenebis-4-salicyloxycoumarin*, m.p. 223—225°, and [Pd–C–AcOH–EtOAc at 1 atm., which has no effect on (**V**)] of (**VII**) gives 4-*salicyloxy-3-phenylcoumarin*, m.p. 185—187°.

V. Michael condensation of 4-hydroxycoumarin (**IX**) with unsaturated ketones, COR·CH:CR′R″, occurs best in boiling C_5H_5N or for CHPh:CH·COMe in boiling H_2O and yields (**IX**) substituted at $C_{(3)}$ by ·CR′R″·CH_2·COR. With CH_2N_2 these give 3-OMe-compounds but they are cyclised by boiling 4% HCl–MeOH and then methylated to yield substances (*A*). Michael condensation with NaOEt, HCl, or piperidine in EtOH leads to mixtures of the primary products with (*A*). Thus are obtained 4-*hydroxy-3-γ-keto-α-methyl-*n-*butyl-* (44%), m.p. 141° [*Me ether*, b.p. 170° (bath)/0·5 mm.], -3-*γ-keto-αα-dimethyl-*n-*butyl-* (**X**) (13%) m.p. 212°, -3-*γ-keto-α-phenyl-*n-*butyl-* (**XI**) (40%), m.p. 161° (*Me ether*, m.p. 127°), -3-*γ-keto-α-*p-*anisyl-*n-*butyl-* (45%), m.p. 160° [*Me ether*, b.p. 240° (bath)/0·5 mm.], -3-*γ-keto-α-4′-hydroxy-3′-methoxyphenyl-*n-*butyl-* (18%), m.p. 181°, -3-*γ-keto-αγ-diphenyl-*n-*propyl-* (37%), m.p. 160° (*Me ether*, m.p. 91°), -3-*γ-keto-α-phenyl-γ-o-hydroxyphenyl-* (**XII**) (34%), m.p. 194°, -*coumarin* and 2-*methoxy-*2 : 4-*dimethyl-* (29%), m.p. 124°, -2 : 4 : 4-*trimethyl-* (80%), m.p. 102°, -4-*phenyl-*2-*methyl-* (**XIII**) (83%), m.p. 166°, -4-p-*anisyl-*2-*methyl-* (75%), m.p. 163°, -4-4′-*hydroxy-*3′-*methoxyphenyl-* (82%), m.p. 187°, -2 : 4-*diphenyl-* (13%), m.p. 205°, and -4-*phenyl-*2-o-*hydroxyphenyl-* (50%), m.p. 194° (decomp.), -3 : 4-*dihydrocoumarino-*3′ : 4′-5 : 6-1 : 2-*pyran*. HCl–H_2O–EtOH converts (**XI**) into 2-*ethoxy-*4-*phenyl-*2-*methyl-*3 : 4-*dihydrocoumarino-*3′ : 4′-5 : 6-1 : 2-*pyran*, m.p. 177°. In boiling HCl–H_2O–MeOH (1 : 5 : 5), (**XIII**) regenerates (**XI**) but in boiling NaOH–H_2O–MeOH (1 : 5 : 5) gives a salt, *o*-CO_2Na·C_6H_4·C<(·O·CMe(OMe)·C(CO₂Na)—)>CHPh, which yields (**XIII**) by ring-closure on acidification. When ketones, *o*-OH·C_6H_4·CH:CH·COR, are used in the Michael condensation, the primary products suffer spontaneous dehydration to (*B*); thus are obtained 4-*acetonyl-* (69%), m.p. 263° (decomp.), 4-*phenacyl-* (76%), m.p. 240° (decomp.), and 4-o-*hydroxyphenyl-coumarino-*4′ : 3′-2 : 3-*benz-*4-*pyrone* (75%), m.p. 241° (decomp.). Dehydration, but without cyclisation, also accompanies formation of (**X**), yielding 34% of 2 : 4-*diketo-*3-*αγ-dimethyl-*Δ*β-butenyl-idenechroman*, m.p. 93°. Structures are proved by synthesis of (**XI**) also from 3 : 3′-benzylidenebis-4-hydroxycoumarin by NaOH. The Michael condensation of (**IX**) fails with CHPh:CH·CO_2Et, CHPh:C(CO_2Et)$_2$, phorone, CO(CH:CHPh)$_2$, or furfurylideneacetone. *o*-OH·C_6H_4·COMe and *o*-OH·C_6H_4·CHO in aq. NaOH at 85° give 2 : 2′-*dihydroxy-β-phenylacrylophenone* (14%), m.p. 160° (decomp.) (*dibenzoate*, m.p. 114°). The primary Michael products and (*A*) have potent anticoagulant properties.



(*A*.)

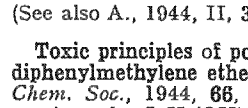


(*B*.)

VI. Treating the appropriate 4-hydroxycoumarins in aq. NaOH (1 mol.) with $AgNO_3$ (1·02 mol.) gives the Ag salts, which with acetobromoglucose (**XIV**) and $CaSO_4$ in C_6H_6 yield *β-4-hydroxy-* (40%), m.p. 178—179°, $[\alpha]_D^{25}$ −63·2° in $CHCl_3$, *β-4-hydroxy-6-methyl-* (36%), m.p. 168—170°, $[\alpha]_D^{25}$ −24·9° in C_6H_6, and *β-4-hydroxy-6-phenyl-coumarin glucoside tetra-acetate* (**XV**) (47%), m.p. 156—158°, $[\alpha]_D^{25}$ −58·4° in C_6H_6, and 3 : 3′-*methylenebis-4-coumarin monoglucoside tetra-acetate* (**XVI**) (25%), sinters at 185° [giving 3 : 3′-methylene-4 : 4′-epoxydicoumarin (**XVII**), m.p. 290°], whence a trace of NaOMe in MeOH yields *β-4-hydroxy-* (90%), m.p. 201—202°, $[\alpha]_D$ −106° in MeOH, and *β-4-hydroxy-6-methyl-coumarin glucoside* (90%), m.p. 223—224°, $[\alpha]_D^{25}$ −86° in C_5H_5N. The free hydroxycoumarin with (**XIV**), $CaSO_4$, and a few drops of quinoline (no yield in absence thereof or in presence of a large amount) in C_6H_6 gives *ββ′-3 : 3′-methylenebis-4-hydroxycoumarin diglucoside octa-acetate* (**XVIII**), m.p. 167—168°, $[\alpha]_D^{30}$ +58·0° in C_6H_6, and 4-*hydroxy-3-7′-coumarino-*4″ : 3″-2′ : 3′-*benzpyranylcoumarin glucoside tetra-acetate*, m.p. 234—235°, $[\alpha]_D^{25}$ −9·0° in C_5H_5N. The glucosides or their acetates reduce Fehling's solution after boiling for a few min. owing to their rapid hydrolysis by alkali which is due to the high acidity of the enol. In Ba(OMe)$_2$–MeOH at room temp. (**XV**) gives 4-hydroxy-3-phenylcoumarin (81%) and α-methylglucoside, and (**XVIII**) gives (**XVII**) (59%). In boiling Ba(OMe)$_2$–MeOH, (**XVIII**) gives 59%, and in boiling NaOMe–MeOH (**XVI**) gives 55—86%, of (**XVII**). The mechanism of the methanolysis is discussed. R. S. C.

Keten acetals. XIV. Reactions of keten acetal with quinones. S. M. McElvain and E. L. Engelhardt (*J. Amer. Chem. Soc.*, 1944, **66**, 1077—1083; cf. A., 1944, II, 130).—Contrary to earlier views (A., 1942, II, 227), quinones and CH_2:C(OEt)$_2$ (**I**) give 4-hydroxy-1-ethoxybenzfurans. Substitution by Me hinders and finally stops the addition. In the benzoquinone series, substitution by Br facilitates reaction which occurs by addition at a nuclear C, but in the naphthaquinone series the Br is partly replaced. The product obtained (*loc. cit.*) from *p*-O:C_6H_4:O by (**I**) is shown to be 4-*hydroxy-1-ethoxybenzfuran*; with Ac_2O it gives a monoacetate and with MgMeI evolves 1 CH_4 without addition; with HBr in dioxan at room temp. (24 hr.) it gives 4-hydroxycoumaran-1-one (**II**) (67%), m.p. 189—191°; in boiling 75% EtOH it gives 2 : 5 : 1-(OH)$_2$$C_6H_3$·$CH_2$·$CO_2$Et (47%), converted into (**II**) by boiling 10% HCl; it is unaffected by (**I**) or $CHMeN_2$, as also is (**II**), but with *iso*-C_5H_{11}·ONa–EtI in boiling *iso*-C_5H_{11}·OH, (**I**) or (**II**) gives 4-*ethoxycoumaran-1-one*, m.p. 89—90°. *p*-OH·C_6H_4·OEt (modified prep.), CH_2:CH·CH_2Br, and K_2CO_3 in $COMe_2$ give *quinol Et allyl ether* (80%), m.p. 39—40°, converted in boiling NPhEt$_2$ into 4-*ethoxy-2-allylphenol* (89·5%), b.p. 184—185°/50 mm., the *acetate*, b.p. 161—162°/1·5 mm., of which with, successively, O_3–AcOH, H_2O_2–AcOH–H_2O, NaOEt–EtOH, and HCl gives (**II**) (14·5%). 1 : 2 : 6 : 4-O:$C_6H_2Me_2$:O (modified prep.) and (**I**) at 150° (not at 125° or in boiling xylene) give a tar containing 7% of 4-*hydroxy-1-ethoxy-*3 : 5-*dimethylbenzfuran*, m.p. 100—101°, hydrolysed by hot 75% EtOH to *Et* 3 : 6-*dihydroxy-*2 : 4-*dimethylphenylacetate*, m.p. 147—148°, whence boiling 25% HCl yields 4-*hydroxy-*3 : 5-*dimethylcoumaran-1-one* (56%), m.p. 143—144°. 1 : 2 : 5 : 4-O:$C_6H_2Me_2$:O (modified prep.) and (**I**) react only at 150°, giving tarry polymers and a small amount of the quinol, which may be derived from 1 : 4 : 2 : 5 : 6-(OH)$_2$$C_6HMe_2$·CH:C(OEt)$_2$. Duroquinone does not react with (**I**). 1 : 4-O:$C_{10}H_6$:O and (**I**) at 90° give a tar containing 2% of 4′-*hydroxy-*4-*ethoxynaphtha-*1′ : 2′-1 : 2-*furan*, m.p. 106—108°, whence boiling 75% EtOH yields 4-*hydroxy-*5 : 6-*benzcoumaran-1-one*, m.p. 204—205°. 1 : 2 : 4-O:C_6H_3Br:O (modified prep.) reacts with (**I**), giving 10% of EtBr and a product whence hot 75% EtOH yields (? 6-)*bromo-*4-*hydroxycoumaran-1-one* (26·5%), m.p. 202—204°, converted by methylation etc. into (? 3-)*bromo-*2 : *o-dimethoxyphenylacetic acid*, m.p. 194—195° (could not be oxidised to ArCO_2H). 1 : 2 : 5 : 4-O:$C_6H_2Br_2$:O and (**I**) in boiling C_6H_6 give, after treatment with 75% EtOH, *Et* 2 : 5-*dibromo-*3 : 6-*dihydroxyphenylacetate* (40%), m.p. 126—127°, but 1 : 2 : 6 : 4-O:$C_6H_2Br_2$:O reacts in Et_2O to give only a tar (a trace of EtBr is formed). 1 : 2 : 4-O:$C_{10}H_5$Br:O (modified prep.) and (**I**) at 125° give EtBr (40%) and a product whence 75% EtOH yields xanthopurpurin Et$_2$ ether (20·6%); the primary product, 1 : 4 : 2-O:$C_{10}H_5$(:O)·CH:C(OEt)$_2$, has reacted with a second mol. of (**I**). 1 : 2 : 3 : 4-O:$C_{10}H_4Br_2$:O (modified prep.) and (**I**) in boiling C_6H_6 give *Et* 3-*bromo-*1 : 4-*naphthaquinone-*2-*acetate* (57·6%), m.p. 124—125°. 1 : 2 : 3 : 4-O:$C_{10}H_4$MeBr:O reacts with (**I**) at 125°, yielding ~25% of EtBr and tars. R. S. C.

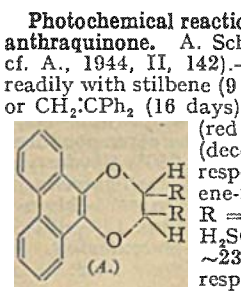
Constitution of trimeric glyoxal. H. Raudnitz (*Chem. and Ind.*, 1944, 327).—"Trimeric glyoxal" is 2 : 3 : 6 : 7-*tetrahydroxy-*1 : 4 : 5 : 8-"*naphthodioxan*" (**I**), formed by way of [CH(OH)$_2$]$_2$. With H_2SO_4 in $COMe_2$, (CHO)$_2$ gives the 2 : 3-6 : 7-(CMe$_2$:)$_2$-*derivative*, m.p. 207° (cf. Fischer *et al.*, A., 1926, 599), of (**I**), which contains no OH or CO and in hot mineral acid regenerates (CHO)$_2$ and $COMe_2$. (See also A., 1944, II, 340.) R. S. C.



(**I**.)

Toxic principles of poison ivy. II. Preparation and properties of diphenylmethylene ethers of pyrocatechols. H. S. Mason (*J. Amer. Chem. Soc.*, 1944, **66**, 1156—1158; cf. A., 1943, II, 447).—Conversion of *o*-C_6H_4(OH)$_2$ (**I**) into its monoallyl ether and thence 3-allylpyrocatechol, m.p. 73—74° (lit. 70—72°), is described. CPh_2Cl_2 and (**I**) in warm C_6H_6 or, best, pinene at 100° (cf. Sachs *et al.*, A., 1904, i, 878) give good yields of *o*-C_6H_4:O_2CPh_2, m.p. 94—94·6°. 3-n-*Propyl-*, m.p. 41·5—42°, and 4-tert-*butyl-pyrocatechol CPh$_2$: ether*, m.p. 138—139°, are similarly prepared. These ethers are readily hydrolysed by dil. boiling HCl–EtOH and disrupted by hydrogenolysis (Pd; EtOH), but are stable to hot 25% KOH–EtOH or MgBu^{a}Br. R. S. C.

Photochemical reactions. VIII. Reaction of ethylenes with phenanthraquinone. A. Schonberg and A. Mustafa (*J.C.S.*, 1944, 387; cf. A., 1944, II, 142).—In sunlight, phenanthraquinone (**I**) reacts readily with stilbene (9 days), styrene (4 days), CPh_2:CHPh (4 days), or CH_2:CPh_2 (16 days) in C_6H_6 to give photo-*products*, m.p. ~260° (red melt) (**II**), m.p. ~130° (decomp.), m.p. ~225° (decomp.) (**III**), or m.p. 202—203° (orange melt), respectively, considered to be 5 : 6-*oo*-diphenylene-2 : 3-dihydro-1 : 4-dioxans, *e.g.*, (**II**) = (*A*), R = Ph. All four products yield (**I**) with conc. H_2SO_4 at room temp.; (**II**) or (**III**) at ~270° or ~235° in CO_2 give (**I**) and stilbene or CPh_2:CHPh, respectively. A. T. P.



(*A*.)

Ichthynone, $C_{23}H_{20}O_7$, m.p. 203—204°, $\alpha \pm 0°$ (contains 2 OMe) [dibromide, m.p. 234—235°; phenylhydrazone, m.p. 195—200° (decomp.); H_2-compound, m.p. 233—234°], from *Ichthyomethia piscipula*.—See A., 1944, III, 708.

Amino-ketones. III. β-Tetrahydro*iso*quinolmo-ketones and [their] derivatives. Reactions with Grignard reagents. N. H. Cromwell and J. S. Burch (*J. Amer. Chem. Soc.*, 1944, **66**, 872—873; cf. A., 1944, II, 352).—Tetrahydro*iso*quinoline with CHPh:CH·COMe or CHPh:CH·COPh in 95% EtOH at, successively, the b.p., room temp., and 0° gives δ-*tetrahydroisoquinolino*-δ-*phenyl*-n-*butan*-β-*one* (**I**) (59%), m.p. 71—72°, and β-*tetrahydroisoquinolino*-β-*phenylpropiophenone* (**II**) (83%), m.p. 90—91° (*oxime*, m.p. 173—175°), respectively. The *oxime* (prep. by NH_2OH,HCl–NaOAc–MeOH–H_2O at, successively, the b.p., room temp., and 0°), m.p. 155—157°, of (**I**) with Na–EtOH gives γ-*amino*-α-*tetrahydroisoquinolino*-n-*butylbenzene* (32%), b.p. 178—180°/1 mm. (*Bz* derivative, m.p. 159—161°). MgPhBr and (**I**) or MgMeI and (**II**) in Et_2O give δ-*tetrahydroisoquinolino*-ββ-*diphenyl*-n-*butan*-β-*ol* (43—45%), m.p. 115—116°. MgMeI and (**I**) give β-*tetrahydroisoquinolino*-β-*phenyl*-tert.-*amyl alcohol* [2-(γ-*hydroxy*-α-*phenyl*-γ-*methyl*-n-*butyl*)*iso*quinoline] (47%), m.p. 95—96°. MgPhBr and (**II**) give β-*tetrahydroisoquinolino*-αaγ-*triphenyl*-n-*propyl alcohol*, m.p. 78—80°. R. S. C.

Interaction of iodine with some ketones in presence of pyridine. L. C. King (*J. Amer. Chem. Soc.*, 1944, **66**, 894—895).—COArAlk (1) and I (1 mol.) in an excess (2 mols. required for the reaction) of C_5H_5N at 100° give 1-phenacyl-, m.p. 215—219°, 1-α-*naphthoylmethyl*-, m.p. 219—220°, 1-*anthroylmethyl*-, m.p. 235—237°, and 1-α-*methylphenacyl-pyridinium iodide*, m.p. 152—153° (derived *perchlorates*, m.p. 189—190°, 176—177°, 227—230°, and 141—142°, respectively), which with NaOH in boiling H_2O or 50% EtOH give BzOH, α-$C_{10}H_7$·CO_2H, 1-anthroic acid, and BzOH, respectively. R. S. C.

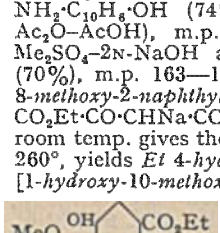
Production of aminosulphanilamidopyridines.—See B., 1944, III, 186.

Excretion of metabolic products of sulphapyridine in the dog. J. V. Scudi (*Proc. Soc. Exp. Biol. Med.*, 1944, **55**, 197—199; cf. A., 1940, III, 758).—Following oral administration of sulphapyridine, a *hydroxysulphapyridine*, m.p. 180—181° (corr.), and a H_2O-sol. *hydroxysulphapyridine glucuronide* [as the *Ag* salt or the *brucine* salt, m.p. 215° (decomp.)] have been isolated from dog urine. F. R. S.

Structure and synthesis of pyridoxamine and pyridoxal. S. A. Harris, D. Heyl, and K. Folkers (*J. Biol. Chem.*, 1944, **154**, 315—316).—Treatment of 3-hydroxy-2-methyl-5-hydroxymethyl-4-methoxymethylpyridine with NH_3 at 120—140° gives the -4-aminomethyl compound (pyridoxamine), m.p. 193—193·5°. Oxidation ($KMnO_4$) of pyridoxine gives an aldehyde, the oxime of which on decomp. with HNO_2 and treatment with EtOH–HCl affords a cyclic acetal. This is hydrolysed to 3-hydroxy-4-formyl-2-methyl-5-hydroxymethylpyridine (pyridoxal). F. R. S.

8-Hydroxyquinaldine as an analytical reagent. L. L. Merritt, jun., and J. K. Walker (*Ind. Eng. Chem.* [*Anal.*], 1944, **16**, 387—389).—Technique for the prep. of 8-hydroxyquinaldine is recorded (cf. C., 1944, Part 4). J. D. R.

Derivatives of 7- and 10-methoxybenz(f)quinolme. A. C. Mueller and C. S. Hamilton (*J. Amer. Chem. Soc.*, 1944, **66**, 860—862).—Stirring 2 : 8-NH_2·$C_{10}H_6$·SO_3H and KOH at 260° gives 2 : 8-NH_2·$C_{10}H_6$·OH (74%), the *N*-Ac derivative (prep. by boiling Ac_2O–AcOH), m.p. 215—216° (lit. 210—211°), of which with Me_2SO_4–2N-NaOH at 30° gives 2-*acetamido*-8-*methoxynaphthalene* (70%), m.p. 163—164°. Boiling conc. aq. HCl–EtOH then gives 8-*methoxy*-2-*naphthylamine hydrochloride* (81%), cryst., which with CO_2Et·CO·CHNa·CO_2Et (**I**) and a drop of conc. HCl in EtOH at room temp. gives the oily anil, which, introduced into mineral oil at 260°, yields *Et* 4-*hydroxy*-6′-*methoxy*-5 : 6-*benzquinoline*-2-*carboxylate* [1-*hydroxy*-10-*methoxybenz*(f)*quinoline*-3-*carboxylate*] (**II**) (61%), m.p. 181—183°. This is hydrolysed by boiling 2N-alkali to the corresponding *acid* (*hydrochloride*, cryst., hydrolyses in H_2O), which at the m.p. (250°) gives CO_2 and 4-*hydroxy*-6′-*methoxy*-5 : 6-*benzquinoline* (**III**) (28%), m.p. 180—182°. Probably owing to steric hindrance the OH in (**III**) could not be replaced by halogen. 2 : 5-NH_2·$C_{10}H_6$·OH, m.p. 198—200° (lit. 199·5°), gives similarly 2 : 5-NHAc·$C_{10}H_6$·OH, +H_2O, m.p. 117—121°, and anhyd., an oil (lit. 100°, 98—99°), and 5-*methoxy*-2-*naphthylamine*, m.p. 71—72°, unstable (N-*Ac* derivative, m.p. 151—152°; *hydrochloride*, cryst.), which with (**I**) etc. gives an anil, converted in mineral oil at 250° into *Et* 4-*hydroxy*-3′-*methoxy*-5 : 6-*benzquinoline*-2-*carboxylate* [cf. (**II**)], m.p. 256—258°, and thence as above into the corresponding *acid*, m.p. 292—295° (decomp.), and (at 295°, later 280°) 4-*hydroxy*-3′-*methoxy*-5 : 6-*benzquinoline* [1-*hydroxy*-7-*methoxybenz*(f)*quinoline*] (55%), m.p. 308—311°. With boiling $POCl_3$ this gives 4-chloro- (74%), m.p. 118—119°, and thence 4-*morpholino*-, m.p. 136—137°, and 4-*piperidino*-, m.p. 116—117°, -3′-*methoxy*-5 : 6-*benzquinoline*. R. S. C.



(II.)

Hydantoins. III. Chemical constitution and hypnotic action. A. Novelli, Z. M. Lugones, and P. Velasco (*Anal. Asoc. Quím. Argentina*, 1942, **30**, 225—231; cf. A., 1941, II, 334).—Intraperitoneal injection in white rats of a no. of substituted hydantoins showed hypnotic action only for 5 : 5-diphenyl-, 5-phenyl-5-ethyl-, and 5-phenyl-5-*n*-propyl-hydantoin. The following are new: 5-*phenyl*-5-*amyl*-, m.p. 125—127°, -5-*hexyl*-, m.p. 140—142°, -3-N-*methyl*-5-n-*propyl*, m.p. 134—135°, -1 : 3-N-*dimethyl*-o-n-*propyl*-, m.p. 92°; 5-p-*tolyl*-5-n-*propyl*-, m.p. 189—190°, -3-N-*methyl*-5-n-*propyl*-, m.p. 116—117°, -1 : 3-N-*dimethyl*-5-n-*propyl*-, m.p. 77—78°; 5-p-*bromophenyl*-5-n-*propyl*-, m.p. 207—208°; 5-cyclo*hexyl*-5-*phenyl*-, m.p. 236—237°; 5 : 5-o-*diphenylene*-3-N-*methyl*-, m.p. 248—250°; 5 : 5-o-*diphenylene*-1 : 3-N-*dimethyl*-, m.p. 205—206°; 5 : o-*diphenyl*-3-N-*methyl*-, m.p. 215°; 5 : 5-o-*phenylenetrimethylene*-1 : 3-N-*dimethyl*-, m.p. 140°, and -3-N-*methyl*-, m.p. 184·5°; 5 : 5-*aminodiphenylene*-, m.p. 310—312°; 5-2′-*phenanthryl*-3-N-*methyl*-5-*ethyl*-, m.p. 189—190°, and -1 : 3-N-*dimethyl*-5-*ethyl*-, m.p. 150°; 5 : 5-2′-*methyl*-o-*isopropyl*cyclo*pentamethylene*-3-N-*methyl*-, m.p. 165°, and -1 : 3-N-*dimethyl*-*hydantoin*, m.p. 117—118°. The m.p. of 5 : 5-2′-methyl-5′-*iso*propyl*cyclo*pentamethylenehydantoin is now recorded as 257°. F. R. G.

1-Methylhistidine. I. Synthesis of *dl*-1-methylhistidine. W. Sakami and D. W. Wilson (*J. Biol. Chem.*, 1944, **154**, 215—222).—4(5)-Hydroxymethylglyoxaline from *d*-fructose is oxidised (HNO_3) to glyoxaline-4(5)-aldehyde, methylated (Me_2SO_4–$COMe_2$) to 1-methylglyoxaline-5-aldehyde, which condenses ($NHEt_2$–C_5H_5N) with 2-thio-3-acetylhydantoin (improved prep.) to 2-*thio*-(1′-*methyl*-5′-*glyoxalinylmethylidene*)*hydantoin*. Reduction and hydrolysis (HI–P) of this compound affords *dl*-1-methylhistidine, isolated as the bis-3 : 4-dichlorobenzenesulphonate, m.p. 251—252°, and identical with the product obtained by hydrolysis of anserine with $Ba(OH)_2$. F. R. S.

***N*-Desylarylamines in Leuckart's reaction.** A. Novelli and J. C. Somaglino (*Anal. Asoc. Quím. Argentina*, 1943, **31**, 147—152).—NHPh·CHPhBz reacts with RCO·NH_2 (R = H, Me, Et) to give the same glyoxaline derivatives as benzoin, NHPh being replaced by NH·COR. 4 : 4′-*Dimethoxy*-N-*desylaniline*, m.p. 115° (from anisoin and NH_2Ph at 140° in CO_2), with HCO·NH_2, and *p*-C_6H_4Me·NH·CHPhBz with NH_2Ac behave similarly. F. R. G.

Abnormal quaternary salts of bispyridinium derivatives of nicotinic acid. J.-A. Gautier and E. Leroi (*Compt. rend.*, 1943, **216**, 619—620).—Nicotinic acid and $[CH_2]_nHal_2$ (n = 2 or 3) give monoacid salts, $(CO_2^-$·$C_5H_4N^+$·$[CH_2]_n$·$N^+C_5H_4$·$CO_2H)Hal^-$, whence $AgNO_3$ gives the dibetaines, CO_2^-·$C_5H_4N^+$·$[CH_2]_n$·$N^+C_5H_4$·CO_2^-. Diacid salts cannot be prepared in this series but are readily formed from pyridine-2- or -4-carboxylic acid. R. S. C.

Synthetic amino-acids. Reactions of 2 : 5-diketo-3 : 6-di-β-chloroethylpiperazine. H. R. Snyder and M. E. Chiddix (*J. Amer. Chem. Soc.*, 1944, **66**, 1000—1002).—2 : 5-Diketo-3 : 6-di-β-chloroethylpiperazine (**I**) (A., 1943, II, 72) loses HCl with great ease. *E.g.*, in boiling NaOH–EtOH it gives 2 : o-*diketo*-3 : 6-*divinylpiperazine* (**II**) (62%), m.p. 192·5° (corr.) (instantaneous) or decomp. >240° (slow heating). Attempts to prepare the $(CN·[CH_2]_2)_2$ compound and to condense (**I**) with $CH_2Ac·CO_2Et$ also led to (**II**), which was either isolated as such or identified after hydrolysis by conc. HCl as α-amino-γ-butyrolactone hydrochloride, m.p. 199—200°. However, some reactions of (**I**) occur normally. Thus, with morpholine or piperidine at 85°, rising to 125°, with KCNS–$COMe_2$ at room temp. and then the b.p. or $CH_2Ph·SH$–NaOEt–EtOH at the b.p. it gives 2 : 5-*diketo*-3 : 6-*di*-β-*morpholino*- (~40%), m.p. 229—232° (corr.), -*piperidino*-, m.p. 242—243° (corr.), -*thiocarbamido*- (~15%), m.p. 207—208° (corr.), or -benzylthiol- (~50%), m.p. 173—174° (corr.) (lit. 165°, 176°), -ethylpiperazine, respectively. R. S. C.

Non-Markovnikov addition in reactions of 2 : 5-diketo-3 : 6-divinylpiperazine. H. R. Snyder and M. E. Chiddix (*J. Amer. Chem. Soc.*, 1944, **66**, 1002—1004).—Non-Markovnikov addition of HCl and RSH occurs with 2 : 5-diketo-3 : 6-divinylpiperazine (**I**) (preceding abstract), probably owing to its ·CH(NH)·CO acting as a *m*-directing group. Thus, gaseous HCl or HBr in AcOH gives 2 : 5-diketo-3 : 6-di-β-chloroethyl- (**II**) and -3 : 6-*di*-β-*bromoethylpiperazine* (**III**), m.p. 221° (decomp.) [reconverted into (**I**) by hot H_2O]. With MeSNa, (**II**) or (**III**) gives methionine anhydride and thence methionine [Bz derivative, m.p. 151—151·5° (lit. 143—145°)]. $CH_2Ph·SNa$ and (**II**) give 2 : 5-*diketo*-3 : 6-*di*-β-*benzylthiolethylpiperazine*, m.p. 177—178°, hydrolysed by boiling aq. HCl to $CH_2Ph·S·[CH_2]_2·CH(NH_2)·CO_2H$, m.p. 226—230° (decomp.) (lit. 190—191°). H_2S and (**I**) in EtOH containing a little AcOH at room temp. gives 2 : 5-*diketo*-3 : 6-*di*-β-*thiolethylpiperazine*, m.p. 185—186° (decomp.), whence hot conc. HCl yields homocysteinethiolactone hydrochloride. M.p. are corr. R. S. C.

Arylamino-heterocyclic compounds. I. Synthetic method. II. Arylaminopyrimidines. C. K. Banks (*J. Amer. Chem. Soc.*, 1944, **66**, 1127—1130, 1131).—I. Heterocyclic compounds containing nuclear "active" halogen react with aromatic amines in H_2O, fastest (5 examples) in 2N-HCl; the reaction is slower in more dil. acid or H_2O and addition of NaOH greatly decreases the rate.

Efficiency is HCl > H_2SO_4 > tartaric acid, but the differences are not large. An excess of HCl causes hydrolysis. An electronic mechanism is suggested. The reaction does not apply to compounds containing N·C:C·Hal nor to aromatic or aliphatic halides.

II. The following are obtained from 4-chloro-2-aminopyrimidine in boiling very dil. HCl. 2-*Amino*-4-*anilino*-*pyrimidine* (**I**), m.p. 155—156° (*Ac*$_n$, m.p. 170°, and *Ac*$_1$ derivative, m.p. 176—178°; *hydrochloride*, m.p. 184—185°), and -6-*methylpyrimidine*, m.p. 170—172°; 2-*amino*-4-p-*carboxyanilino*-, m.p. 295—297° (decomp.) (*diethylaminoethyl* ester *trihydrochloride* and *Na* salt, m.p. >250°), -4-o- (*dihydrochloride*, m.p. indefinite, >200°), -4-*m*- (*hydrochloride*, m.p. 178—180°), and -4-p-*hydroxyanilino*-, m.p. 245—247° (decomp.) (*hydrochloride*, m.p. 275—277°), -4-2′ : 6′-dihydroxyanilino- (*dihydrochloride*, m.p. 123—124°), -4-*p*-anisidino- (*hydrochloride*, m.p. 276—278°), -4-3′ : 4′-dimethoxyanilino- (*hydrochloride*, m.p. 270°), -4-*p*-acetamidoanilino- (*dihydrochloride*, m.p. 299—300°), -4-*p*-acetylanilino- (*hydrochloride*, m.p. 275—276°), -4-m-2′-*xylidino*-, m.p. 186—187°, -4-p-, m.p. 193—195°, and -4-o-*xenylamino*-, m.p. 130—132°, -4-α-*naphthylamino*-, m.p. 133—134°, and -4-*morpholino*-, m.p. 157—161°, -*pyrimidine*. 4-Amino-2-anilino- (*hydrochloride*, m.p. 149—150°) and 2 : 4-*dianilino*-*pyrimidine*, m.p. 136—138° (*hydrochloride*, m.p. 194—195°), are similarly obtained. (**I**) has pressor action on anæsthetised dogs equal to that of benzedrine but of shorter duration. R. S. C.

Hydrogenation of basic nitriles in presence of Raney nickel. W. Huber (*J. Amer. Chem. Soc.*, 1944, **66**, 876—879).—Hydrogenation of basic heterocyclic nitriles in presence of Pd–ZrO_2, Pd–C, or PtO_2 in Ac_2O, HCl–EtOH, H_2SO_4–EtOH, HCl–AcOH, or H_2SO_4–AcOH at 25—55°/55—80 lb. is slow and gives much *sec.*-amine. In presence of Raney Ni and 3—4 mols. of NH_3 in MeOH or, less well, EtOH, Pr$^{\beta}$OH, BuOH, dioxan, Bu$^{a}_2$O, or HCO·NH_2 at 60—200 lb. it is rapid (30—80 min. for 0·5 mol.) and gives excellent yields of primary with 0—5% of *sec.*-amine; vigorous shaking is essential; use of <2·5 mols. of NH_3 increases the amount of *sec.*-amine. Details are given for hydrogenation of 4-amino-2-methyl- and 2 : 4-diaminopyrimidine-5-nitrile, 4-phenyl-1-benzylpiperidine-4-nitrile, pyridine-3-nitrile, 4-methyl-5-cyanomethylthiazole, NEt$_2$·[CH$_2$]$_3$·CN, and furan-3-nitrile. The following are incidentally described: 4-*phenyl*-1-*benzyl*-4-*aminomethylpiperidine*, m.p. 71—72°, b.p. 224—226°/1 mm. [*dihydrochloride*, m.p. 202—204° (decomp.)]; di-2-methyl-4-amino-5-pyrimidylmethylamine [*tetrahydrochloride*, m.p. 357° (decomp.); (? tetra)picrate, m.p. 269—270° (decomp.)], which, when formed in presence of NH_3–Ni, is often hydrolysed to 4-amino-2-methyl-5-hydroxymethylpyrimidine; *di*-δ-*diethylaminobutylamine*, b.p. 125—126°/2 mm. (hygroscopic hydrochloride; *tripicrate*, m.p. 90—93°). R. S. C.

***d*-Ribobenziminazole. A correction.** G. R. Barker, (Miss) K. R. Cooke, and J. M. Gulland (*J.C.S.*, 1944, 339).—The properties of *d*-ribobenziminazole (cf. A., 1944, II, 85) are now shown to be in agreement with those described by Richtmeyer *et al.* (cf. A., 1942, III, 248). F. R. S.

Some aminopyridoquinolines and their quaternary salts. R. D. Haworth and W. O. Sykes (*J.C.S.*, 1944, 311—314).—8-*Bromo*-6-*aminoquinoline*, m.p. 148° [*hydrochloride* (+2H$_2$O), m.p. >275°; Ac derivative, m.p. 199°], prep. by reduction (SnCl$_2$–HCl) of the NO_2-compound, with *m*-NO_2·C_6H_4·SO_3H (Skraup) gives 7-bromo-6 : 5-2′ : 3′-pyridoquinoline, m.p. 147—149° (lit. 150°) [*hydrochloride*, m.p. >325°; *monomethiodide*, m.p. 305° (decomp.)], which with aq. NH_3 (sealed tube at 180—200°) affords the 7-NH_2-compound, m.p. 213—215° [*methochloride* (+H$_2$O), m.p. 272° (decomp.); *Ac* derivative, m.p. 188°, and its *methiodide* (+H$_2$O), m.p. 283° (decomp.)]. 4 : 1 : 3-$C_6H_3Br(NH_2)_2$ (improved prep. through the *diformyl* derivative, m.p. 179—180°) with *m*-NO_2·C_6H_4·SO_3H (Skraup) yields 8-bromo-5 : 6-2′ : 3′-pyridoquinoline (*monohydrochloride*, m.p. 268—274°), aminated to the 8-NH_2-compound (**I**), [*hydrochloride*, m.p. 295° (decomp.)], also obtained from the 8-OH-compound [*dihydrochloride*, m.p. 315° (decomp.)], which is prepared from 5-amino-8-hydroxyquinoline sulphate (Skraup). The Ac derivative of (**I**), m.p. 198° (lit. 201°), is methylated with difficulty using *p*-C_6H_4Me·SO_2Me; after hydrolysis (HCl), 8-*amino*-5 : 6-2′ : 3′-*pyridoquinoline methochloride hydrochloride* (+H$_2$O), m.p. 280° (decomp.), is obtained. F. R. S.

Action of formamide on the arylacetonitriles. I. A. Novelli (*Anal. Asoc. Quím. Argentina*, 1943, **31**, 23—31).—PhCN, heated with NH_4HCO_3 and HCO_2H, yields NH_2Bz. CH_2Ph·CN similarly gives CH_2Ph·CO·NH_2, together with 2-*benzyl*-1 : 3 : 5-*triazine*, m.p. 155—156° [*hydrochloride*, blackens 220°, m.p. 225—226°; *methiodide*, softens 158°, m.p. 172°; *mercurichloride*, m.p. 185—187°; *picrate*, decomp. ~198°, m.p. 207° (decomp.)], which is oxidised ($KMnO_4$) to BzOH. 1-$C_{10}H_7$·CH_2·CN similarly gives 1-$C_{10}H_7$·CH_2·CO·NH_2 together with 2-α-*naphthyl*-1 : 3 : 5-*triazine*, softens 190°, m.p. 193—194·5° [*methiodide*, m.p. 282° (decomp.); *mercurichloride*, m.p. 195—197°; *picrate*, m.p. 205° (decomp.)]. F. R. G.

Hydantoins. II. Dihydantoins. A. Novelli (*Anal. Asoc. Quím. Argentina*, 1941, **29**, 181—184).—(COPh·[CH$_2$]$_n$)$_2$ (*n* = 2 or 3) with NaCN and NH_4HCO_3 yield αδ-*di*-[5-(5-*phenylhydantoinyl*)]*butane*, m.p. 291—292·5°, and α*ζ*-*di*-[5-(5-*phenylhydantoinyl*]*hexane*, m.p. 260—265°, which have no hypnotic action on rats. F. R. G.

Experiments on the synthesis of purine nucleosides. V. Coupling of pyrimidine derivatives with diazonium salts. Method for the preparation of 5-aminopyrimidines. B. Lythgoe, A. R. Todd, and A. Topham. **VI. Synthesis of 9-*d*-xylosido-2-methyladenine and of 6-*d*-xylosidamino-2-methylpurine.** J. Baddiley, B. Lythgoe, and A. R. Todd (*J.C.S.*, 1944, 315—317, 318—322).—V. In order to introduce a 5-NH_2-group into 6-amino-4-glycosidaminopyrimidines which would preclude hydrolysis of the sugar linkage, 4 : 6-diaminopyrimidines have been coupled with diazonium compounds, giving 5-azo-compounds; catalytic hydrogenation of these products yields 4 : 5 : 6-triaminopyrimidines. $CH_2(CN)_2$ in EtOH–H_2O–NaOAc with diazotised *p*-NO_2·C_6H_4·NH_2 gives *p-nitrobenzeneazomalononitrile*, m.p. 222° (decomp.); the p-*Cl*-compound (**I**), m.p. 188—190° (decomp.), is similarly prepared. 4 : 6-Diaminopyrimidine with diazotised *p*-NO_2·C_6H_4·NH_2 and aq. $NaHCO_3$ affords 4 : 6-*diamino*-5-p-*nitrobenzeneazo*-2-*methylpyrimidine*, m.p. >360°, reduced (H_2–Ni) to the 4 : 5 : 6-(NH_2)$_3$-compound (**II**), m.p. 252—254°, also obtained by reducing the 4 : 6-*dianimo*-5-*benzeneazo*-derivative, m.p. 311° (decomp.), from benzeneazomalononitrile and acetamidine hydrochloride (**III**). 4 : 6-Diamino-6-methylpyrimidine with diazotised *p*-C_6H_4Cl·NH_2 yields 4 : 6-*diamino*-o-p-*chlorobenzeneazo*-2-*methylpyrimidine*, m.p. 340—342° (decomp.), also obtained from (**I**) and (**III**). 4 : 6-*Diamino*-5-p-*chlorobenzeneazopyrimidine*, m.p. 301—302° (decomp.), reduced to (**II**), and the -5-p-NO_2-compound, m.p. >360°, are similarly prepared. 4-Methyluracil is similarly converted into 2 : 6-*dihydroxy*-5-p-*chlorobenzeneazo*-4-*methylpyrimidine*, m.p. 235° (decomp.). The structural conditions governing the coupling of pyrimidine derivatives and their relation to those governing nitrosation are surveyed.

VI. Diazotised *p*-NO_2·C_6H_4·NH_2 in aq. $NaHCO_3$ with 6-amino-4-*d*-xylosidamino-2-methylpyrimidine gives 6-*amino*-4-d-*xylosidamino*-5-p-*nitrobenzeneazo*-2-*methylpyrimidine*, m.p. 230° (decomp.), which on hydrogenation (H_2–Ni) affords a mixture of the corresponding 5-aminopyrimidine with *p*-$C_6H_4(NH_2)_2$. 6-*Amino*-4-d-*xylosidamino*-5-(2′ : 4′-*dichlorobenzeneazo*)-2-*methylpyrimidine* (**IV**) (+ 2·5H$_2$O), m.p. 218—219° (decomp.), similarly prepared with HCS_2Na following hydrogenation, yields the 6-*amino*-5-*thioformamido*-4-d-*xylosidamino*-derivative (+H$_2$O), m.p. 232° (decomp.), which gives only small amounts of purine. Acetylation (Ac_2O–C_5H_5N) of (**IV**) leads to 6-*amino*-4-*triacetyl*-d-*xylosidamino*-5-(2′ : 4′-*dichlorobenzeneazo*)-2-*methylpyrimidine*, decomp. ~230°, which after hydrogenation and treatment with HCS_2H gives the 6-*amino*-5-*thioformamido*-4-*triacetyl*-d-*xylosidamino*-compound, m.p. 148° (decomp.); this with boiling C_5H_5N in N_2 affords (loss of H_2S) a mixture of 6-*triacetyl*-d-*xylosidamino*-2-*methylpurine* (+C_5H_5N), m.p. 204—205° [deacetylated to 6-d-*xylosidamino*-2-*methylpurine* (**V**), m.p. 218° (decomp.), $[\alpha]_D^{19}$ −32° in H_2O], and 9-d-*xylosido*-2-*methyladenine* (**VI**), m.p. 288° (decomp.), $[\alpha]_D^{19\cdot5}$ −26° in H_2O. (**V**) could not be deaminated by HNO_2, but its hydrolysis (0·1N-H_2SO_4) product, 2-methyladenine (**VII**), is deaminated to 2-*methylhypoxanthine*, m.p. >360°, indicating that in (**V**) the xylose residue is present in a 6-xylosidamino-group. Methylation (MeOH–NaOMe–MeI) of (**VII**) affords 2 : 7-, m.p. 338° (decomp.), and 2 : 9-*dimethyladenine* (**VIII**), m.p. 238°, required for purposes of comparison with (**V**). 6-*Amino*-4-*methylamino*-2-*methylpyrimidine*, m.p. 239—240°, obtained from the corresponding 4-Cl-compound and NH_2Me, with diazotised *p*-C_6H_4Cl·NH_2 gives the -5-p-*chlorobenzeneazo*-derivative, m.p. 207° (decomp.), which after hydrogenation and treatment with HCS_2Na leads to 6-*amino*-5-*thioformamido*-4-*methylamino*-2-*methylpyrimidine*, m.p. 189° (decomp.), cyclised to (**VIII**). Hydrolysis (N-H_2SO_4) of (**VI**) affords (**VII**) and *d*-xylose, and deamination (HNO_2) of it gives 9-d-*xylosidamino*-2-*methylhypoxanthine* (+H$_2$O), m.p. 203°. Ultraviolet absorption spectra of (**V**), (**VI**), (**VII**), and (**VIII**) and its 2 : 7-analogue are compared. F. R. S.

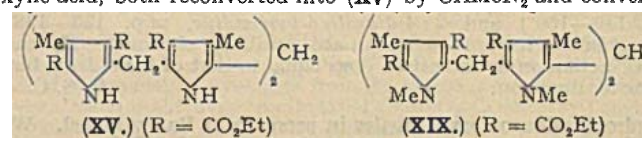
Convenient preparation of synthetic xanthopterin. J. R. Totter (*J. Biol. Chem.*, 1944, **154**, 105—108).—Reduction (Na–Hg) of leucopterin gives Na dihydroxanthopterin, which with $AgNO_3$ affords xanthopterin and with HCl yields dihydroxanthopterin, both in good yield. F. R. S.

Pyrrole series. XII. Condensation of pyrroles with bromine. Self-oxidation and a new type of displacement reaction. A. H. Corwin and P. Viohl. **XIII. Anomalous reaction of dipyrrylmethanes leading to a new class of heterocyclic compounds.** A. H. Corwin and R. C. Ellingson. **XIV. Formation of dipyrrolopyridones in the course of a proposed porphyrin synthesis.** A. H. Corwin and S. R. Buc (*J. Amer. Chem. Soc.*, 1944, **66**, 1137—1146, 1146—1151, 1151—1156; cf. A., 1944, II, 276).—XII. Et 2 : 4-dimethylpyrrole-3-carboxylate (**I**) and Br in MeOH at −60° or, less well, KOH–MeOH at 0—10° give the 5-Br-derivative (**II**), which with Br [best (75·3%), 4 atoms] in AcOH at 10—15° gives *Et*$_2$ 3 : 5 : 4′-*trimethyl*-5′-*bromodi*-2-*pyrrylmethene*-4 : 3′-*dicarboxylate hydrobromide* (**III**), m.p. 153° (decomp.), also obtained from (**I**) by Br in Et_2O–AcOH at −5° to 0°. Bromination of (**I**) is much faster than that of (**II**). Contrary to Fischer's view, formation of (**III**) thus proceeds: (**I**) + 2Br →

(II) + HBr; (II) + Br→Et 2-bromo-3-methyl-5-bromomethylpyrrole-4-carboxylate (IV) + HBr; (II) + (IV)→(III). Formation of (III) is limited by a HBr-catalysed self-oxidation of (II) to yield HBr and Et_2 3 : 5 : 3′ : 5′-tetramethyldi-2-pyrrylmethene-4 : 4′-dicarboxylate (V) [derived base (VI), decomp. 190°], so that the rate of evolution of HBr exceeds that of consumption of Br by (II); in accordance with this view, (II) contains active Br, liberating I from KI. Two reaction mechanisms are discussed, each being partly supported by the following reactions. Et_2 3 : 5 : 3′ : 5′-tetramethyldi-2-pyrrylmethane-4 : 4′-dicarboxylate [obtained from (VI) by hydrogenation], m.p. 230° (slight decomp.), (II), and a little HBr in dioxan at room temp. give (VI). The free base from (III) with (I) in Et_2O at 0° gives *Et* 5″-*bromo*-3 : 5 : 3′ : 5′ : 4″-*pentamethyltri*-2-*pyrrylmethane*-4 : 4′ : 3″-*tricarboxylate* (VII) (95·5%), m.p. 210° (decomp.), whence HCl–Et_2O at 0° or HBr–AcOH at 40° and then aq. NH_3 regenerates the base from (III) (73% and 43%, respectively). Et 3-bromo-4-methyl-2-bromomethylpyrrole-5-carboxylate and (II) in AcOH at 40° give, after treatment with NH_3, *Et* 3′-*bromo*-2 : 5 : 4′-*trimethyldi*-2-*pyrrylmethene*-4 : 5′-*dicarboxylate*, m.p. 135—136° (decomp.). However, Et_2 3-methyl-5-bromomethylpyrrole-2 : 4-dicarboxylate does not condense with (II). (III), (I), and a little HBr in AcOH at 50° give (V). H_2–Pd–C at 2 atm. reduces (VII) to *Et* 3 : 5 : 3′ : 5′ : 4″-*pentamethyltri*-2-*pyrrylmethane*-4 : 4′ : 3″-*tricarboxylate*, m.p. 224—225°. 3-*Carbethoxy*-4-*methylpyrrole*-5-*carboxylic acid* (prep. from the Et_2 ester by KOH in boiling 80% EtOH), m.p. ~230° (evolution of CO_2), in boiling glycerol yields Et 3-methyl- (46%), m.p. 73°, and thence Et 2-formyl-3-methyl-pyrrole-4-carboxylate, m.p. 122°, which with (I) and HCl in Et_2O at 0° and then aq. NH_3 yields Et_2 3 : 5 : 3′-trimethyldi-2-pyrrylmethene-4 : 4′-dicarboxylate (VIII), m.p. 147° (decomp.). The hydrobromide of (VIII) with Br–AcOH at 50° and then aq. NH_3 gives *Et* 5′-*bromo*-3 : 5 : 3′-*trimethyldi*-2-*pyrrylmethene*-4 : 4′-*dicarboxylate*, m.p. 151° (decomp.). (VIII), (I), and a trace of $KHSO_4$ in Et_2O give *Et* 3 : 5 : 3′ : 5′ : 3″-*pentamethyltri*-2-*pyrrylmethane*-4 : 4′ : 4″-*tricarboxylate*, decomp. 222°.

XIII. Treating 3-carbalkoxydi-2-pyrrylmethanes with alkali (Na; $NaCPh_3$ in dioxan; NaOAlk) gives 6-keto-1 : 2 : 3 : 6-tetrahydropyrrolo-2′ : 3′-4 : 5-pyridino-1 : 2-1″ : 2″-pyrroles ["dipyrrolo-(1 : 2-*a*,2′ : 3′-*d*)pyridine-4(9)-one"; this numbering is as (*A*)], which fluoresce like lubricating oil. For this condensation the 1′-N must be unsubstituted and at least as acidic as ; 1-N is the more acidic, the alkali reacts at this point and ring-closure of the 3-CO_2Alk with the 1′-N is impossible. Mixed m.p. in this series are unreliable and re-esterification in presence of NaOAlk is very facile, so that care is essential in identification. Structures assigned below are held to be proved by the reactions of the isomerides. The compound, m.p. 204°, obtained (A., 1943, II, 72) from Et_3 1 : 4 : 3′ : 5′-tetramethyldi-2-pyrrylmethane-3 : 5 : 4′-tricarboxylate (IX) by Na, is Et_2 6-*keto*-1′ : 4′ : 3″ : 5″-*tetramethyl*-1 : 2 : 3 : 6-*tetrahydropyrrolo*-2′ : 3′-4 : 5-*pyridino*-1 : 2-1″ : 2″-*pyrrole*-5′ : 4″-*dicarboxylate* (X). The violet-red colour formed in alkali is due to carbenium salt formation. (X) is unaffected by conc. H_2SO_4, HCl–EtOH at 0°, boiling H_2SO_4–AcOH–H_2O, or ketone reagents. 3-Carbomethoxy-5-carbethoxy-2 : 4-dimethylpyrrole (prep. from $CHMeAc{\cdot}CO_2Me$, $OH{\cdot}N{:}CAc{\cdot}CO_2Et$, Zn dust, and NaOAc in aq. AcOH at 90°, rising to 110°; 68% yield), m.p. 130—131°, with Na in PhMe at 98—110° and then Me_2SO_4 at 90° gives 3-*Me* 5-*Et* 1 : 2 : 4-*trimethylpyrrole*-3 : 5-*dicarboxylate* (76%), m.p. 78—80°, whence SO_2Cl_2 yields 4-*Me* 2-*Et* 1 : 3-*dimethyl*-5-*chloromethylpyrrole*-2 : 4-*dicarboxylate*, m.p. 69—71° (and a by-product, m.p. 85—87°). With (I) in boiling MeOH this gives 3-*Me* 5 : 4′-Et_2 1 : 4 : 3′ : 5′-*tetramethyldi*-2-*pyrrylmethane*-3 : 5 : 4′-*tricarboxylate* (XI) (82%), m.p. 139°, whence $NaCPh_3$ in dioxan yields (X), m.p. 197—199° or, after longer reaction, 189—190°; the difference in m.p. is due to partial re-esterification and pure (X) is obtained by treating this product with NaOEt. Et_2 1 : 3-dimethyl-5-chloromethylpyrrole-2 : 4-dicarboxylate and (I) in hot MeOH give 4′-*Me* 3 : 5-Et_2 1 : 4 : 2′ : 5′-*tetramethyldi*-2-*pyrrylmethane*-3 : 5 : 4′-*tricarboxylate* (84%), m.p. 134°, whence $NaCPh_3$ in dioxan gives 4″-*Me* 5′-*Et* 6-*keto*-1′ : 4′ : 3″ : 5″-*tetramethyl*-1 : 2 : 3 : 6-*tetrahydropyrrolo*-2′ : 3′-4 : 5-*pyridino*-1 : 2-1″ : 2″-*pyrrole*-5′ : 4″-*dicarboxylate*, m.p. 194°. $OH{\cdot}N{:}CAc{\cdot}CO_2Me$ (prep. described) with $CH_2Ac{\cdot}CO_2Et$ etc. as above gives 5-carbomethoxy-3-carbethoxy-2 : 4-dimethylpyrrole (54%), m.p. 164°, and thence as above the 1 : 2 : 4-Me_3 ester, m.p. 86—87°, and 2-*Me* 4-*Et* 1 : 3-*dimethyl*-5-*chloromethylpyrrole*-2 : 4-*dicarboxylate* (82%), m.p. 99—100°. This with (I) in MeOH yields 5-*Me* 3 : 4′-Et_2 1 : 4 : 3′ : 5′-*tetramethyldi*-2-*pyrrylmethane*-3 : 5 : 4′-*tricarboxylate* (58%), m.p. 130—131°, which with $NaCPh_3$ in dioxan yields impure 5′-*Me* 3″-*Et* 6-*keto*-1′ : 4′ : 3″ : 5″-*tetramethyl*-1 : 2 : 3 : 6-*tetrahydropyrrolo*-2′ : 3′-4 : 5-*pyridino*-1 : 2-1″ : 2″-*pyrrole*-5′ : 3″-*dicarboxylate* (XII), m.p. 188—189°, obtained pure (m.p. 210—211°) by treatment with NaOMe. With NaOMe, (IX) or (XI) gives (X), and with NaOEt either gives pure (XII).

XIV. Et_4 4 : 4-dimethyldi-2-pyrrylmethane-3 : 5 : 3′ : 5′-tetracarboxylate (XIII) with 1 mol. of NaOH in hot EtOH gives 58% of Na_1 and some Na_2 salt, separated by extraction with H_2O and fractional pptn. therefrom by NaCl; 2 mols. of NaOH lead to mainly the Na_2 salt. Et_3 4 : 4′-*dimethyldi*-2-*pyrrylmethane*-3 : 5 : 3′-*tricarboxylate*-5′-*carboxylic acid* [with $CHMeN_2$ yields (XIII)] in glycerol + a little quinoline at 240° (or 285°) gives Et_3 4 : 4′-*dimethyldi*-2-*pyrrylmethane*-3 : 5 : 3′-*tricarboxylate* (XIV) (86·5%), m.p. 187° (and ? an *isomeride*, m.p. 184—185°), which with CH_2O–conc. HCl–EtOH at the b.p. gives the *substance* (XV), m.p. 216—217° (decomp.), whence NaOH yields no cryst. acid. With 1 mol. of NaOH in hot EtOH, (XIV) gives a small yield of an acid, m.p. >205°, which in hot glycerol yields a substance, m.p. >250°. With 0·05 mol. of NaOH in hot aq. EtOH, (XIV) gives Et_2 6-*keto*-4′ : 4″-*dimethyl*-1 : 2 : 3 : 6-*tetrahydropyrrolo*-2′ : 3′-4 : 5-*pyridino*-1 : 2-1″ : 2″-*pyrrole*-5 : 3″-*dicarboxylate* (34%), darkens 235°, decomp. 245°. Condensation of Et_2 4 : 4′-dimethyldi-2-pyrrylmethane-3 : 3′-dicarboxylate by NaOH (1 mol.) in boiling 60% EtOH and heating the product in glycerol gives 6-*keto*-4 : 4″-*dimethyl*-1 : 2 : 3 : 6-*tetrahydropyrrolo*-2′ : 3′-4 : 5-*pyridino*-1 : 2-1″ : 2″-*pyrrole* (poor yield), cryst. Partial hydrolysis of the Et_4 ester (XVI) gives the 3 : 3′-Et_2 and 3 : 3′ : 5′-Et_3 ester of 1 : 4 : 1′ : 4′-tetramethyldi-2-pyrrylmethane-3 : 5 : 3′ : 5′-tetracarboxylic acid, both reconverted into (XV) by $CHMeN_2$ and converted



(XV.) (R = CO_2Et) (XIX.) (R = CO_2Et)

by heating in glycerol + a little quinoline into Et_2 1 : 4 : 1′ : 4′-*tetramethyldi*-2-*pyrrylmethane*-3 : 3′-*dicarboxylate* (XVII), m.p. 164—165°, and Et_3 1 : 4 : 1′ : 4′-*tetramethyldi*-2-*pyrrylmethane*-3 : 5 : 3′-*tricarboxylate* (XVIII), m.p. 127—129°, respectively. With paraformaldehyde and a little AcOH in boiling BuOH, (XVIII) yields the *substance* (XIX) (89%), m.p. 147—149°. Partial hydrolysis of (XVIII) gives an acid [reconverted into (XVIII) by $CHMeN_2$], decarboxylation of which gives (XVII). R. S. C.

Amino-ketones. II. Synthesis of αβ-diamines from α-amino-ketones. N. H. Cromwell and H. Hoeksema (*J. Amer. Chem. Soc.*, 1944, **66**, 870—871; cf. A., 1943, II, 108).—ω-*Morpholinoacetophenoxime* (prep. from the ketone by NH_2OH,HCl–KOH–H_2O–MeOH at 20°), m.p. 147—149°, with H_2–Raney Ni in EtOH at 50° (NH_3 inhibits reduction) gives 10%, with H_2–Pd–C–AcOH gives 15%, with H_2–Pd–C–HCl–AcOH gives 10%, or with Na–EtOH gives 26% of β-*morpholino*-α-*phenylethylamine* (I), b.p. 134°/2 mm. ω-*Piperidinoacetophenoxime*, *forms*, m.p. 117—118·5° and 136—138·5°, with Na–EtOH gives 24% of β-*piperidino*-α-*phenylethylamine* (II), b.p. 128°/3 mm. No diamine is obtained by catalytic hydrogenation of β-amino-ketoximes, probably owing to loss of the β-amino-radical to give unsaturated oximes. Low yields of (I) and (II) by Na–EtOH are due partly to loss of NH_3 during distillation of the product. *Bz* derivatives, m.p. 143—144° and 135—136°, of (I) and (II), respectively, are potent local anæsthetics. R. S. C.

Phenylthiocarbamides. Contribution to the study of the triad –N·C·S–. XIII. Action of sulphur monochloride on *N*-phenyl-*N*-methylthiocarbamide. Formation of thiodiazoles. R. Sahasrabudhey and H. Krall (*J. Indian Chem. Soc.*, 1944, **21**, 17—18).—The compound formed by the interaction of S_2Cl_2 with a $CHCl_3$ solution of $NPhMe{\cdot}CS{\cdot}NH_2$ is 2-imino-3-methyl-2 : 3-dihydrobenzthiazole and not either of the compounds suggested by Dost (A., 1906, i, 351). $NHPh{\cdot}CS{\cdot}NH_2$ gives 2-aminobenzthiazole under the same conditions. C. R. H.

Vasosulpha compounds. W. F. Hamilton, M. F. George, jun., E. Simon, and F. M. Turnbull (*J. Amer. Pharm. Assoc.*, 1944, **33**, 142—145; cf. A., 1944, III, 756).—Dissolution of the appropriate ephedrine alkaloid and sulpha drug in warm, dil., aq. Na_2SO_3, followed by cooling, yields *ephedronium sulphathiazole*, m.p. 206°, and *sulphadiazine*, m.p. 192—193°, and *deoxyephedronium sulphathiazole*, m.p. 118—120°, and *sulphadiazine*, m.p. 187—189° (all m.p. corr.). F. O. H.

Organo-metallic derivatives of methylbenzthiazole. Magnesium compounds. C. Courtot and S. Tchelitcheff (*Compt. rend.*, 1943, **217**, 201—203).—The Mg compound from methylbenzthiazole with CO_2 gives *benzthiazolylacetic acid*, m.p. 112—113°, with $COMe_2$ forms *benzthiazolylmethyldimethylcarbinol*, m.p. 79°, with some benzthiazolylmethyl alcohol, and with $COPh_2$, *diphenylbenzthiazolylmethylcarbinol*, m.p. 194—195°, is obtained. F. R. S.

Organo-metallic derivatives of methylbenzthiazole and of benzthiazole. C. Courtot and S. Tchelitcheff (*Compt. rend.*, 1943, **217**, 231—233).—Methylbenzthiazole reacts with $NaNH_2$ to give the *Na* derivative, which with the appropriate reagent yields: 2-β-phenylethylbenzthiazole, with some dibenzylbenzthiazolylmethane (CH_2PhCl); 2-*n*-amylbenzthiazole, b.p. 152—153°/15 mm., and methyldibutylbenzthiazole, b.p. 176°/15 mm. ($Bu^{\alpha}Cl$); methyl*iso*butylbenzthiazole, b.p. 167°/15 mm. ($Bu^{\beta}Cl$); 2-*iso*hexylbenzthiazole, b.p. 172—175°/25 mm. ($C_5H_{11}Br$); α-benzthiazolyl-Δ-butene, b.p. 153°/15 mm., and δ-benzthiazolyl-$\Delta^{\alpha\zeta}$-heptadiene, b.p. 198°/15 mm., m.p. 126° ($CH_2{:}CH{\cdot}CH_2Br$); and 2-*p*-nitro- and -amino-

phenylbenzthiazole (p-$C_6H_4Cl{\cdot}NO_2$). The *Li* derivative of methylbenzthiazole with *cyclo*hexyl chloride gives benzthiazolyl*cyclo*hexylmethane, b.p. 189—190°/15 mm. (picrate, m.p. 118°), and with $C_2H_4Cl_2$ yields αδ-dibenzthiazolylbutane, m.p. 87° (picrate, m.p. 92—93°). F. R. S.

Derivatives of phenothiazine. H. Gilman and D. A. Shirley (*J. Amer. Chem. Soc.*, 1944, **66**, 888—893).—Phenothiazine (**I**), o-$C_6H_4I{\cdot}NO_2$, Cu-bronze, and K_2CO_3 in boiling xylene give 10-o-*nitro*- (44%), m.p. 156—157°, reduced by Sn–HCl to 10-o-*amino-phenylphenothiazine* (95%), m.p. 139—139·5°, which with the hygroscopic hydrochloride, m.p. 64—68° (lit. 62—64°), of $NEt_2{\cdot}[CH_2]_3{\cdot}Cl$ (prep. from the alcohol by $SOCl_2$–$CHCl_3$; b.p. 73—75°/20 mm.) at 130—140° gives 10-o-γ-*diethylamino*-n-*propylaminophenylphenothiazine* (49%), b.p. 215—230°/<0·5 mm. Similarly are prepared 10-3′-*nitro*-p-*tolyl*-, m.p. 179·5—180°, 10-3′-*amino*-p-*tolyl*-, m.p. 140—140·5°, 10-3′-γ-*diethylamino*-n-*propylamino*-p-*tolyl*-, b.p. 270° (bath)/<0·5 mm., 10-3′-*nitro*-p-*anisyl*-, m.p. 184—186°, 10-3′-*amino*-p-*anisyl*-, m.p. 180—181°, 10-3′-γ-*diethylamino*-n-*propylamino*-p-*anisyl*-, b.p. 220—235°/<0·5 mm., 10-3′-*nitro*-o-*anisyl*-, m.p. 159—160°, 10-4′-*chloro*-2′-*nitrophenyl*-, m.p. 185—186·5°, 10-4′-*chloro*-2′-*aminophenyl*-, m.p. 125·5—126°, and 10-4′-*chloro*-2′-γ-*diethylamino*-n-*propylaminophenyl*-, b.p. 270—280°/2 mm., -*phenothiazine*. With LiBuᵅ and then p-$C_6H_4Me{\cdot}SO_2{\cdot}[CH_2]_2{\cdot}Cl$ in Et_2O, (**I**) gives 10-β-chloroethylphenothiazine (47%), m.p. 96—97° (5-*oxide*, m.p. 154—155°), which with the appropriate amine and Cu-bronze at the b.p. gives 10-β-*diethylamino*- (67%), b.p. 161—165°/<0·5 mm., 10-β-*di*-n-*propylamino*-, b.p. 225—230°/1 mm., 10-β-*morpholino*-, m.p. 74·5—75·5°, b.p. 198—201°/<0·5 mm., and 10-β-6′-*methoxy*-8′-*quinolylamino*- [prep. by Cu powder at 140—150° (N_2)], m.p. 118·5—119·5°, -*ethylphenothiazine*. 10-γ-*Chloro*-, m.p. 60°, 10-γ-*diethylamino*- (**II**), b.p. 170—182°/<0·5 mm. (*dipicrate*, m.p. 103—104°), 10-γ-*di*-n-*propylamino*-, b.p. 257—265°/1—2 mm., 10-γ-*diallylamino*-, b.p. 245—260°/1 mm., and 10-γ-*piperidino*-, b.p. 255—265°/1—2 mm., -n-*propylphenothiazine* are similarly prepared. p-$OMe{\cdot}C_6H_4{\cdot}NHPh$ (prep. from p-$OMe{\cdot}C_6H_4{\cdot}NHAc$ by PhBr, Na_2CO_3, and Cu powder, followed by hydrolysis). m.p. 106° (lit. 105°), S, and a little I at 140—150° and later 175° give 3-methoxyphenothiazine (45—51%), m.p. 158—159° (lit. 163°, 159°) (*Ac* derivative, m.p. 121—122·5°), which affords, as above, 3-methoxy-10-γ-chloro-, an oil, -10-γ-*di*-n-*propylamino*-, b.p. 250—265°/2 mm., and -10-γ-*diethylamino*-n-*propylphenothiazine*, b.p. 220—225°/<0·5 mm. p-$C_6H_4Me{\cdot}NHPh$, S, and a little I at 280° give 3-*methylphenothiazine*, m.p. 166—168°. Conc. HNO_3 converts 10-acetyl- or 10-ethyl-phenothiazine in AcOH into 3 : 7-dinitro-10-acetyl-, m.p. 265—267° (cf. lit.), and 3-*nitro*-10-*ethyl-phenothiazine* 5-*oxide*, m.p. 204·5—205°, respectively. AlkBr, (**I**), Cu powder, and Na_2CO_3 in boiling C_6H_6 gives 10-*allyl*-, b.p. 187—195°/1 mm., or at 170—180° 10-n-*decyl*-, b.p. 183—185°/<0·5 mm. (3-NO_2-derivative 5-*oxide*, m.p. 102·5—103°), and 10-n-*octadecyl-phenothiazine*, m.p. 53° (5-*oxide*, m.p. 98°). 10-*Phenyl*-, m.p. 170—171°, and 3-*nitro*-10-*phenyl-phenothiazine* 5-*oxide*, m.p. 223·5—224·5°, are also prepared. (**I**), its 10-alkylaminoalkyl and 10 other derivatives have no effect on avian malaria, except that (**II**) is doubtfully active in 12·5-mg. doses. Phenothiazine derivatives have very slight toxicity to canaries. R. S. C.

Metallation of 10-phenyl- and 10-ethyl-phenothiazine. H. Gilman, P. R. Van Ess, and D. A. Shirley (*J. Amer. Chem. Soc.*, 1944, **66**, 1214—1216).—10-Ethylphenothiazine (**I**) (prep. from phenothiazine (**II**) and Et_2SO_4 in EtOH at 120—130°; 56% yield], m.p. 101—103°, with LiBuᵅ in Et_2O–N_2 and then CO_2 gives 6% of 10-*ethylphenothiazine*-4- (or -2-)*carboxylic acid*, m.p. 178—179° (*Me* ester, m.p. 111—112°), converted by boiling, conc. HI into m-$C_6H_4Ph{\cdot}CO_2H$, m.p. 138—139°, which is also obtained (m.p. 140°; 2·5% yield) from m-$C_6H_4I{\cdot}CO_2Me$ by K_2CO_3 and Cu-bronze in boiling NH_2Ph and then boiling 15% KOH–EtOH. The 3-Hg·OAc derivative, m.p. 151—153°, of (**I**) with aq. NaCl gives the HgCl derivative, which in I–KI–H_2O–CCl_4 gives 3-*iodo*-10-*ethylphenothiazine* (80%), m.p. 126—127°, whence MgBuᵅBr–I and then CO_2 gives 10-*ethylphenothiazine*-3-*carboxylic acid*, m.p. 197·5—198·5°. 10-Phenylphenothiazine [prep. from (**II**) by PhI, Cu powder, and Na_2CO_3 at the b.p.], m.p. 94·5°, with LiBuᵅ and then CO_2 gives 10-*phenylphenothiazine*-4-(or -2-)*carboxylic acid* (9·5%), m.p. 258—258·5° (*Me* ester, m.p. 133—134°), converted by boiling, conc. HI into m-$CO_2H{\cdot}C_6H_4{\cdot}NPh_2$. 10-p-, m.p. 221—221·5° (*Me* ester, m.p. 140·5—141·5°), and 10-m-*carboxyphenylphenothiazine*, m.p. 254—255° (*Me* ester, m.p. 98—99°), are also obtained from (**II**) by p- and m-$C_6H_4I{\cdot}CO_2Et$, respectively, with Cu powder and K_2CO_3, followed by aq. NaOH or HCl–MeOH. R. S. C.

Total synthesis of 2 : 3 : 4 : 5-tetrahydrobiotin. L. C. Cheney and J. R. Piening (*J. Amer. Chem. Soc.*, 1944, **66**, 1040—1041).—Preliminary data are given for the following reactions. $Cl{\cdot}[CH_2]_3{\cdot}Br + CH_2(CO_2Et)_2 \rightarrow Cl{\cdot}[CH_2]_3{\cdot}CH(CO_2Et)_2 \rightarrow Cl{\cdot}[CH_2]_4{\cdot}CO_2Et \rightarrow$ *Et*$_2$ n-*pentane*-αα′γ-*tricarboxylate*, b.p. 165—170°/4 mm. → the *tricarboxylic acid*, m.p. 82° → ($SOCl_2$; decarboxylation) *α-chloropimelic acid*, m.p. 89—90° → ($SH{\cdot}[CH_2]_2{\cdot}CO_2H$; esterific- *β-carboxyethyl* αε-*dicarbethoxy*-n-*amyl sulphide*, b.p. 210—213 /3 mm. → (Dieckmann) *Et*$_2$ 3-*ketotetrahydrothiophen*-4-*carboxylate*-2-*valerate* → *oxime* → (dry HCl) *Et*$_2$ 3-*aminothiophen*-4-*carboxylate*-2-*valerate*, m.p. 43—44° → 3-*amino*-4-*carbethoxythiophen*-2-*valeric acid*, m.p. 97—97·5° → the N-*Bz* derivative, m.p. 126·5—127·5° → the *hydrazide*, m.p. 140—141° the *azide*, decomp. 99—100° (boiling EtOH) 3-*benzamido*-4-*carbethoxyamino*-2-*thienylvaleric acid*, m.p. 156·5—157·5° → (hydrolysis; $COCl_2$) 2′-*keto*-2′ : 3′-*dihydroglyoxalino*-4′ : 5′-1 : 2-*thiophen*-4-*valeric acid*, m.p. 253—254° (decomp.), the absorption spectrum of which [max. at 260 mμ. (ε 17 × 10^{-3})] resembles those of 2′-*keto*-4-γ-*phenoxy*-, m.p. 174—174·5°, -*benzyloxy*-, m.p. 127—127·5°, and -*hydroxy*-n-*propyl*-2′ : 3′-*dihydroglyoxalino*-4′ : 5′-1 : 2-*thiophen*, m.p. 138—139°. R. S. C.

Hemicyanine dyes.—See B., 1944, II, 244.

VII.—ALKALOIDS.

Pyrolysis of nicotine to myosmine. C. F. Woodward, A. Eisner, and P. G. Haines (*J. Amer. Chem. Soc.*, 1944, **66**, 911—914).—Pyrolysis of nicotine over SiO_2 chips gives NH_3, NH_2Me, HCN, C_5H_5N, 3-methyl-, 3-ethyl-, and 3-vinyl-pyridine, 3 : 2′-nicotyrine, myosmine (**I**), and higher-boiling products. At 555—570° up to 18·1% of (**I**) is obtained, but the yield is much less at 700° or over activated Al_2O_3 at 500°. R. S. C.

Erythrina alkaloids. XIV. Isolation and characterisation of erysothiovine and erysothiopine, new alkaloids containing sulphur. K. Folkers, F. Koniuszy, and J. Shavel, jun. (*J. Amer. Chem. Soc.*, 1944, **66**, 1083—1087; cf. A., 1943, II, 74).—After removal of free alkaloids, the light petroleum extract of *E. glauca* seeds in H_2O gradually yield *erysothiovine* (**I**), $C_{20}H_{23}O_7NS$, $+H_2O$ (lost at 140°/vac.), m.p. 187°, $[\alpha]_D$ +208° in EtOH, and, more slowly at 0°, *erysothiopine* (**II**), $C_{19}H_{21}O_7NS$, $+H_2O$ (lost at 100°/vac.), m.p. 168—169°, $[\alpha]_D^{25}$ +194° in EtOH. In hot 1—2% mineral acid, (**I**) gives erysovine (**III**) and $CO_2H{\cdot}CH_2{\cdot}SO_3H$ (**IV**) (NH_2Ph, m.p. 187—189°, and *sulphapyridine* salt, m.p. 162—163°). Hydrolysis of (**II**) similarly gives erysopine (**V**). The ester group of (**I**) and (**II**) contains the combined SO_3H of (**IV**), since the Ca and Ba salts of (**IV**) are insol. and those of (**I**) and (**II**) are sol. (**I**) is isolated also from *E. pallida*, Britton & Rose, and *E. poeppigiana*. No " thio "-alkaloid is isolated from *E. sandwicensis*, Deg. Threshold doses for curare action (frog) are: erysonine 100, erysodine 15, (**V**) 4, (**III**) 3, (**I**) and (**II**) 1 mg. per kg. body wt. R. S. C.

Alkaloids of the Leguminosæ. VIII. Alkaloids of *Podalyria* species. IX. Isolation of β-phenylethylamine from *Acacia* species. X. Isolation of anagyrine from *Cytisus linifolius* Lam. XI. Alkaloids of the genera *Cytisus* and *Genista*. XII. Alkaloids of *Calycotome spinosa* (L.) Link. XIII. Isolation of tryptamine from some *Acacia* species. E. P. White (*New Zealand J. Sci. Tech.*, 1944, **25**, B, 137—138, 139—142, 143—146, 146—151, 152—157, 157—162).—VIII. Lupanines (**I**) are extracted (Soxhlet) from three species of *Podalyria*, determined by titration, the optical isomerides separated by hot hexane, and identified by m.p. of methiodides, perchlorates, and aurichlorides, alone and mixed with authentic specimens. *P. sericea*, R. Br., tops and seeds contain *d*-(**I**) with less *dl*-, *P. buxifolia*, Willd., *dl*- with a trace of *l*-, and *P. calyptrata*, Willd., pure *l*-, $[\alpha]_D$ −79° in EtOH.

IX. The alkaloids are extracted in a Soxhlet apparatus, or by repeated soaking with 5% HCl with intermittent heating. The tops of eight species forming a distinct morphological group (uninerval phyllodes and flowers in racemes) contain relatively high concns. of $Ph{\cdot}[CH_2]_2{\cdot}NH_2$ (**II**); their seeds contain only traces. The tops of three other species contain traces of (**II**) and small amounts of another alkaloid not yet purified. 20 other species are alkaloid-free. (**II**) is identified by m.p. of its hydrochloride, *mercurichloride* (165°), *mercuri-iodide* (182°), picrate, and aurichloride, alone and mixed with specimens synthesised from $CH_2Ph{\cdot}CN$. Substances allied to (**II**) have previously only been found in low concns. (mainly in parasites and fungi), and are possible intermediates in the biogenesis of tetrahydroisoquinoline alkaloids.

X. Soxhlet extraction of the seeds of *Cytisus linifolius*, Lam., gives ~1% of cytisine (**III**), while the tops yield ~1% of anagyrine (**IV**), with ~0·1% of other bases. The alkaloids are identified by analysis and m.p. of their salts, alone and mixed with authentic specimens, and by slide reactions. (**IV**) gives slide reactions with $KCdI_3$, $AuCl_3$, $HgCl_2$, K_2HgI_4, $AuBr_3$, picric acid, KI_3, and $KBiI_4$.

XI. The genera *Cytisus* and *Genista* can be divided into six groups according to their alkaloid contents: (i) sparteine (**V**) only, (ii) mainly (**I**), with or without some (**V**), (iii) (a large group) (**III**) or allied bases, with no (**V**), (iv) (**III**) or allied bases, with (**V**), (v) calycotomine, sometimes with traces of other alkaloids, (vi) alkaloid-free.

XII. Soxhlet extraction of the seeds of *Calycotome spinosa* with 2% AcOH in 50% EtOH yields ~1% of bases; tops contain only traces. The chief component, named *calycotomine* (**VI**), $C_{10}H_9(OMe)_2(NH)(OH)$, m.p. 139—141°, $[\alpha]_D^{20}$ +21° in H_2O, forms a *hydrochloride*, m.p. 193°, $[\alpha]_D$ +15° in H_2O, a *picrate monohydrate*, m.p. 163—166°, a *perchlorate*, m.p. 176—177°, a *mercurichloride*, m.p. 118—119°, a *Bz*$_2$ derivative, m.p. 120—122°, and a nitrosoamine. Methylation with CH_2O and HCO_2H gives the N-*Me*

derivative (**VII**) (*hydrochloride*, m.p. 216°), with MeI, the *hydriodide* of (**VII**), m.p. 228—229°, and with Me_2SO_4 and NaOH, quaternary material. (**VI**) itself has no phenolic reactions, but demethylation gives an *o*-dihydric phenol (intense green colour with $FeCl_3$). (**VI**) gives characteristic slide reactions, particularly with $AuBr_3$, KI_3, picric acid, $HgCl_2$, and $KCdI_3$. It reacts negatively for *C*-Me and for indole, whilst $KMnO_4$–NaOH oxidation gives an insol. *substance*, $C_{11}H_{11}O_4N$, m.p. 316°, blue-fluorescent in EtOH, and two other fractions, all containing N and OMe. Traces of *dl*-(**VI**) (*hydrochloride*, m.p. 193°) are also present. Another trace alkaloid is named *calycotamine* (*hydrochloride*, $C_{11}H_{15-17}O_3N$,HCl, m.p. 206°, $[\alpha]_D$ +20° in H_2O); it has 2 OMe and no NMe, like (**VI**), but is distinct from it.

XIII. *Acacia floribunda* tops contain up to 0·2% of a mixture of (**II**) and tryptamine (3-ω-aminoethylindole) (**VIII**); flowers contain up to 1%, whilst *A. pruinosa* tops contain 0·04%. *A. longifolia* flowers and tops contain up to 0·2% of alkaloids, including (**II**), but not (**VIII**). (**VIII**) is identified by the reactions characteristic for 3-substituted indoles, by its m.p. and that of its hydrochloride and picrate (alone and mixed with specimens synthesised by reduction of the product from Mg indolyl iodide and $CH_2Cl{\cdot}CN$), and by slide reactions (particularly with $KBiI_4$ and picric acid). It has not formerly been found in plants. S. A. M.

Antiplasmodial action and chemical constitution. VII. Derivatives of quinine and *iso*quinine. T. S. Work (*J.C.S.*, 1944, 334—335).—Reduction of crude quininal, obtained by ozonolysis of quinine, with H_2–Pd–C, gives quinonol, isolated as the dihydrobromide (*monosulphate*, m.p. 149°). Decomp. of the ozonide of β-*iso*quinine with H_2O affords 3-*acetyl*-6′-*methoxyrubanol*, m.p. 198—200°, reduced catalytically to the 3-OH·$[CH_2]_2$ derivative (*dihydrobromide*, m.p. 192—194° (decomp.)], which is a diastereoisomeride of the substance previously obtained (cf. Henry *et al.*, A., 1937, II, 266). Although active, none of the compounds showed antiplasmodial action equal to that of quinine. F. R. S.

Quaternary salts of scopolamine.—See B., 1944, III, 169.

Ultra-violet absorption spectrum of ibogaine.—See A., 1944, I, 212.

Aconite alkaloids. XV. Nature of the ring system and character of the nitrogen atom. L. C. Craig, L. Michaelis, S. Granick, and W. A. Jacobs (*J. Biol. Chem.*, 1944, **154**, 293—304).—Hydrolysis (1·056N-NaOH) of delphinine gives *delphonine* (**I**) a resin, m.p. 76—78°; *pyrodelphonine* (**II**) and *α-ketodelphonine* (**III**) are similarly obtained. MeI and (**I**), followed by removal of I with Ag_2O, afford *N-methyl*-de-*delphonine* (**IV**). Aconine, (**I**), heteratisine, and tetrahydroatisine in solution as bases all show a strong absorption between 2200 and 2600 A, and it appears probable that the absorption must be due to a conjugated unsaturation of some kind, indicating that the ring structure of the aconite alkaloids, at least in the form of free bases, could be of tetracyclic character. The hydrochlorides of these bases absorb in a manner which could be ascribed possibly to a single double bond as modified by the N and OH groups present. (**III**) is a cyclic amide and shows an absorption spectrum very similar to that of (**I**) in alkaline solution. The absorption spectrum of (**IV**) indicates the presence of an additional double bond. That of (**II**) indicates a new double bond but different in arrangement from that of (**IV**). F. R. S.

Synthesis of *ON*-dimethylanalobme. L. Marion (*J. Amer. Chem. Soc.*, 1944, **66**, 1125—1127).—The following reactions are recorded. $CHAr{:}CH{\cdot}CO_2H$ (Ar = 3 : 4 : 1-CH_2O_2:C_6H_3) (electrolytic) $Ar{\cdot}[CH_2]_2{\cdot}CO_2H$ (65·2%) → (PCl_5; aq. NH_3) $Ar{\cdot}[CH_2]_2{\cdot}CO{\cdot}NH_2$ (use of $SOCl_2$ leads to β-x-*chloro*-3 : 4-*methylenedioxyphenylpropionamide*, m.p. 146°) → $Ar{\cdot}[CH_2]_2{\cdot}NH_2$ (**I**) (51·3%) {picrate, m.p. 180·5° [lit. 174° (uncorr.)]}. *m*-Cresol → 5 : 1 : 2-$OH{\cdot}C_6H_3Me{\cdot}NO_2$ → 5 : 1 : 2-$OMe{\cdot}C_6H_3Me{\cdot}NO_2$ (18%) → 2 : 5 : 1-$NO_2{\cdot}C_6H_3(OMe){\cdot}CH_2{\cdot}CO{\cdot}CO_2H$ (78%), m.p. 137° → (H_2O_2–NaOH) 2-*nitro*-5-*methoxyphenylacetic acid*, m.p. 178·5°. With PCl_5–$CHCl_3$ and then (**I**) in $CHCl_3$–aq. NaOH, this yields 2-*nitro*-5-*methoxyphenylacet*-β-3′ : 4′-*methylenedioxyphenylethylamide*, m.p. 188°, converted by PCl_5 in $CHCl_3$ into 6 : 7-*methylenedioxy*-1-2′-*nitro*-5′-*methoxybenzyl*-3 : 4-*dihydro*isoquinoline, m.p. 168°, the *methiodide*, m.p. 205°, of which with Zn dust in hot aq. HCl gives 6 : 7-*methylenedioxy*-1-2′-*amino*-5′-*methoxybenzyl*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline *dihydrochloride* (65—74%), m.p. 268°. By diazotisation, heating, and then treating with Zn dust in hot HCl this gives *dl-ON*-dimethylanalobine, an oil [*hydrochloride*, m.p. 266° (decomp.); *picrate*, m.p. 226°], the *methiodide*, m.p. 241°, of which in hot alkali yields *ON*-dimethylanalobinemethine, m.p. 100° (*picrate*, m.p. 258°) (cf. Manske, A., 1938, II, 298). R. S. C.

Alkaloid $C_{17}H_{13-15}(OH)(OMe)N$, m.p. 238°, $[\alpha]_D^{24}$ −77·47° in $CHCl_3$ (benzoate, m.p. 124—125°), and alkaloid $C_{17}H_{13}(OMe)_4N,0{\cdot}5H_2O$, m.p. 152·5—153°, $[\alpha]_D^{24}$ −214·22° in EtOH, −187·93° in $CHCl_3$ [picrate, m.p. 242—245°; styphnate, m.p. 247—249°; methiodide, m.p. 273—274° (decomp.)], from *Argemone hispida*.—See A., 1944, III, 707.

VIII.—ORGANO-METALLIC COMPOUNDS.

Aromatic mercury salts.—See B., 1944, III, 169.

Zinc alkyls from *sec.*-alkyl halides. H. Soroos and M. Morgana (*J. Amer. Chem. Soc.*, 1944, **66**, 893—894).—Adding 1 : 1 $Pr^{\beta}Br$–$Pr^{\beta}I$ to Zn–Cu initially at 50° and later maintained at 20° gives an oil, (?) $ZnPr^{\beta}Hal$, which at 90—200°/1 mm. (liquid N_2 trap) gives 85% of $ZnPr^{\beta}_2$, for which $\log P = 7{\cdot}987 - 1858/(t + 230)$. A similar reaction, initiated at 60° and continued at 25°, gives 72% of *Zn di-sec.-butyl*, b.p. 56°/4 mm. The products inflame in air and decompose slowly in diffused light with deposition of Zn. R. S. C.

IX.—PROTEINS.

Electrophoretic evidence for complex formation in casein.—See A., 1944, III, 763.

Optical constants of zinc insulin crystals. G. L. Keenan (*J. Amer. Pharm. Assoc.*, 1944, **33**, 183—184).—Published data are reviewed. Standard reference samples of cryst. insulin showed a crystal habit of a cube or rhombohedron with twinning. Birefringence was positive and vals. of n were n_ϵ 1·562 and n_ω 1·550 (both ±0·002). F. O. H.

Aromatic sulphonic acids as reagents for peptides. Partial hydrolysis of silk fibroin. W. H. Stein, S. Moore, and M. Bergmann (*J. Biol. Chem.*, 1944, **154**, 191—201).—By determining the approx. solubilities of a no. of aromatic sulphonates of various peptides it was shown that these salts could be used to ppt. peptides selectively. The acid hydrolysis of silk fibroin was followed by the Van Slyke HNO_2 and the ninhydrin methods, and after 40 hr. contained ~75% of dipeptides. From this mixture glycyl-*l*-alanine was pptd. as the 2 : 5-dibromobenzenesulphonate, and then *l*-alanylglycine as the 2 : 6-di-iodophenol-4-sulphonate. J. F. M.

Protein–formaldehyde reaction. I. Collagen. E. R. Theis. **II. Wool.** E. R. Theis and M. M. Lams (*J. Biol. Chem.*, 1944, **154**, 87—97, 99—103).—I. Collagen (**I**) and CH_2O were allowed to react in 0·1N-KCl, for 72 hr. at 20°, the pH being adjusted by addition of either HCl or NaOH. The mixture was then analysed for N content, for bound acid or base, and for fixed CH_2O. The results show that fixation of CH_2O with (**I**) in no way affects the acid-binding capacity of (**I**) but does affect the base-binding capacity. No shift in the isoionic point could be shown to be due to CH_2O fixation. Correlation between data for shrinkage temp. and CH_2O fixation is shown.

II. Purified wool keratin (**II**) was treated as in Part I (KOH in place of NaOH) with and without CH_2O. The acid- and base-binding capacity curve without CH_2O is similar to the titration curves obtained by other workers. The acid- and base-binding capacity of CH_2O-treated (**II**) shows no change in the acid zone or at the zero combination point. The CH_2O fixation by (**II**) is given and is somewhat similar to that obtained for (**I**). An interpretation of the data is given. F. R. S.

Action of 1 : 2-epoxides on proteins. H. Fraenkel-Conrat (*J. Biol. Chem.*, 1944, **154**, 227—238).—Epoxides, such as $(CH_2)_2O$, propylene oxide, and epichlorohydrin, are suitable reagents for the esterification of protein CO_2H groups in aq. solution at room temp. Through treatment of cryst. egg-albumin and β-lactoglobulin with these compounds, preps. of modified protein have been obtained, which differ from the original material in that their isoelectric points are shifted as much as 3 pH units towards the alkaline side and they contain considerably fewer CO_2H, phenolic, NH_2, and SH groups than the untreated proteins. The only property of the proteins not appreciably affected by the treatment is the no. of their total basic groups. F. R. S.

Chemical nature of blood-proteins. I—III.—See A., 1944, III, 716.

X.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Esters of lignin derivatives. J. C. Clark and F. E. Brauns (*Paper Trade J.*, 1944, **119**, *TAPPI Sect.*, 53—56).—Treatment with the acyl chloride in C_5H_5N at room temp. or 70—85° gives the *benzoates* and *p-toluenesulphonates* of alkali spruce lignin *A* (**I**), PhOH spruce lignin *A* (**II**), and PhOH Willstatter spruce lignin (**III**). The *undecoate* of (**I**) and *propionate*, *butyrate*, *valerate*, and 3 : 5-*dinitrobenzoate* of (**III**) are similarly prepared. Ac_2O–C_5H_5N gives the acetates. PhNCO in dioxan at the b.p. gives *phenylurethanes*. Analyses indicate introduction of 4—5 aliphatic but 4 aromatic (except 5 Bz) acyl groups into (**I**), 7—8 groups into (**II**), and 5 groups into (**III**). An additional OH group may be formed from (**I**) by fission of an O-ring by alkali. R. S. C.

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A II—Organic Chemistry.

DECEMBER, 1944.

I.—ALIPHATIC.

Physical properties of aliphatic compounds.—See A., 1944, I, 242.

Free radicals in polymerisation processes.—See A., 1944, I, 287.

Catalytic aromatisation of branched-chain aliphatic hydrocarbons. V. I. Komarewsky and W. C. Shand (*J. Amer. Chem. Soc.*, 1944, **66**, 1118—1119).—Aliphatic hydrocarbons containing a quaternary C, which does not permit direct aromatisation, are dehydrocyclised in presence of Cr_2O_3–Al_2O_3 catalysts to aromatic hydrocarbons, indicating that isomerisation occurs during dehydrocyclisation. Dehydrocyclisation of aliphatic hydrocarbons having a structure which allows cyclisation in > one way takes place by a mechanism permitting their direct formation. W. R. A.

Properties of synthetic lubricants. I. Synthesis and properties of λ-*n*-decyldocosane. S. Klos, E. Neuman-Piljat, and S. Piljat (*J. Appl. Chem. Russ.*, 1940, **13**, 1369—1374).—λ-n-*Decyldocosane*, b.p. 233—235°/1 mm., is obtained by reduction (H_2–Ni at 240—245°) of the alcohol derived from Et laurate and *n*-$C_{10}H_{21}$·MgBr. J. J. B.

Application of infra-red absorption spectra to determination of structure of aliphatic ethylenic hydrocarbons.—See A., 1944, I, 236.

Thermal polymerisation and cyclic dimerisation of *iso*butylene. J. B. McKinley (*Univ. Pittsburgh Bull.*, 1944, **40**, 185—194).—Polymerisation of *iso*butene at 365—430°/1280—5350 lb. per sq. in. gives a liquid (yield up to 81%) from which a cyclic dimer, 1 : 1 : 3-*trimethylcyclopentane* (**I**), b.p. 105·0° (yield up to 23%), is obtained on fractionation. 1-Hydroxy-1 : 3-dimethyl*cyclo*pentane (from 2-methyl*cyclo*pentanone) with dry HCl at 2° gives 1-*chloro*-1 : 3-*dimethyl*cyclo*pentane*, b.p. 33·2°/15 mm., which with $ZnMe_2$ or MgMeI yields (**I**) for comparison. The effect of variables on the polymerisation and its mechanism are discussed. D. G.

α-Bromo-Δ$^{\beta}$-heptene. R. Delaby and J. Hubert (*Bull. Soc. chim.*, 1943, [v], **10**, 573—575; cf. A., 1937, I, 282).—On fractionating the product obtained from vinylbutylcarbinol, PBr_3, and C_5H_5N, pure $CHBu^{\alpha}$:$CH·CH_2Br$ (**I**) (*trans*), b.p. 73—74°/19 mm., is isolable, and fractions of b.p. ~60—63°/19 mm. contain some $CHBu^{\alpha}Br·CH$:CH_2; Raman spectra of the fractions are examined. (**I**) and Na–Et_2O yield Δ$^{\alpha}$-tetradecadiene, b.p. 111—114°/15 mm. (liquid bromide) (cf. Prevost *et al.*, A., 1932, 40). A. T. P.

Co-polymerisation of acetylene and butylene in silent electric discharge. A. D. Petrov and D. N. Andreev (*J. Appl. Chem. Russ.*, 1940, **13**, 1341—1347).—Δ$^{\alpha}$-Octene and branched $C_{12}H_{26}$ to $C_{16}H_{34}$ are found in the polymerisate of Δ$^{\alpha}$-butene (**I**). Co-polymerisation of C_2H_2 and (**I**) gives 30% of hydrocarbons boiling at <130° and containing acetylenic hydrocarbons, and 70% of higher-boiling hydrocarbons which at 200° are transformed into a porous rubber-like mass. J. J. B.

Aliphatic nitro-compounds. XV. Nitrations with nitryl chloride. W. Steinkopf and M. Kühnel (*Ber.*, 1942, **75**, [*B*], 1323—1330).—The action of NO_2Cl on a variety of unsaturated compounds is described. C_2H_4 and NO_2Cl give only $C_2H_4Cl_2$ and NO_2. Slow addition of NO_2Cl to well-cooled CH_2:$CHBr$ yields *α-chloro-α-bromo-β-nitroethane*, b.p. 76—77°/15 mm. (:$CHCl)_2$ at 100° yields *ααβ-trichloro-β-nitroethane*, b.p. 63°/13 mm. (yield 65%); similarly CCl_2:$CHCl$ and C_2Cl_4 afford *αααβ-tetrachloro-*, b.p. 76°/18 mm., and *αααββ-pentachloro-*, m.p. 192° (sealed capillary), *-β-nitroethane*. Styrene affords *α-chloro-β-nitro-β-phenylethane*, b.p. 78°/13 mm., in small yield in C_6H_6 whereas in Et_2O it gives styrene *ψ*-nitrosite, m.p. 133° (lit 129°). Similarly $(CHPh$:$)_2$ in C_6H_6 yields *α-chloro-β-nitro-αβ-diphenylethane*, m.p. 220° (decomp.), in C_6H_6 but in Et_2O gives $(CHPhCl)_2$, m.p. 189—193°. *α-Chloro-β-nitro-β-phenylpropionic acid*, m.p. 162—163°, is formed from $CHPh$:$CH·CO_2H$ and NO_2Cl in CCl_4 at 100°. CPh_2:CH is transformed by NO_2Cl in dry Et_2O into unstable, non-cryst. *α-chloro-β-nitro-β-phenylethylene*, which cannot be distilled unchanged under 12 mm.; in the absence of solvent the reactants explode very violently. Alternate passage of keten and NO_2Cl into well-cooled Et_2O leads to $CH_2Cl·COCl$ and small amounts of *nitroacetyl chloride*, b.p. 68°/12 mm., m.p. ~—35° (prolonged distillation easily leads to explosions); on exposure to air is transformed into $MeNO_2$, HCl, and CO_2 and is transformed by NH_3 in Et_2O into $NO_2·CH_2·CO·NH_2$, m.p. 102—103°. C_6H_6 at 20° is converted into 1-*chloro*-2-*nitro*cyclo*hexadiene*, b.p. 21°/12 mm., m.p. ~—30°, which passes into $PhNO_2$ when exposed to air. In Et_2O *cyclo*hexene adds NO_2Cl vigorously, giving 1-*chloro*-2-*nitro*cyclo*hexane*, b.p. 122°/9 mm. $CH_2Cl·NO_2$, b.p. 122—123°, is obtained from CH_2N_2 and NO_2Cl in Et_2O at 0°. *Et chloronitroacetate*, b.p. 88°/0·04 mm., is obtained in small yield with $CH_2Cl·NO_2$ from $CHN_2·CO_2Et$ in well-cooled Et_2O. $NO_2·CH_2·CO_2K$ is smoothly transformed by Cl_2 in H_2O into *dichloronitromethane*, b.p. 106—107°. Gradual addition of saturated K_2CO_3 to a mixture of CH_2O and $CH_2Cl·NO_2$ in H_2O affords $NO_2·CHCl·CH_2·OH$, converted by PCl_5 into *αβ-dichloro-α-nitroethane*, b.p. 124°/10 mm., and by $SOCl_2$ into *di-β-chloro-β-nitroethyl sulphite*, b.p. 147°/10 mm. $CCl_3·CO_2H$ and $CH_2Cl·CN$ at 135° yield *trichloroacetylchloroacetamide*, m.p. 96°. PhOH and NO_2Cl in cold Et_2O give only *o*-$NO_2·C_6H_4·OH$ whereas at room temp. the product is 2 : 4 : 6 : 1-$NO_2·C_6H_2Cl_2·OH$. PhOMe and NO_2Cl afford a very unstable *adduct*, b.p. 32°/12 mm., which loses Cl and N, leaving PhOMe. Solid $C_{10}H_8$ reacts very vigorously with NO_2Cl, giving a mixture of 1-$C_{10}H_7Cl$ and 1-$C_{10}H_7·NO_2$. H. W.

Electrochemical oxidation of *n*-butyl alcohol.—See A., 1944, I, 289.

Preparation of silicon tetrachloride and its use as a basis for obtaining silicic acid esters.—See A., 1944, I, 291.

Action of chromia catalyst on aliphatic *iso*-alcohols and -aldehydes. V. I. Komarewsky and L. G. Smith (*J. Amer. Chem. Soc.*, 1944, **66**, 1116—1117).—At atm. pressure in presence of Cr_2O_3 *iso*-$C_5H_{11}·OH$ forms $COBu^{\beta}_2$ by a condensation–dehydrogenation (*c–d*) process. *iso*Alcohols, having an α-substituted C, give no (*c–d*) reactions but are dehydrogenated to the corresponding aldehydes which remain unaffected at even relatively high pressures. $Bu^{\beta}CHO$ at higher pressure is converted into βζ-dimethyl-Δ$^{\gamma}$-heptene and at atm. pressure into $COBu^{\beta}_2$ in presence of Cr_2O_3. These results support the aldol mechanism. W. R. A.

Substituted acetylenes. XLVII. Acetylenic alcohols from αβ-unsaturated aldehydes and ketones. G. F. Hennion and D. J. Lieb (*J. Amer. Chem. Soc.*, 1944, **66**, 1289—1290; cf. A., 1944, II, 29). —1 : 2-Addition of CH·CNa to compounds containing C:C·CO (cf. Jones *et al.*, A., 1943, II, 53) occurs in Et_2O–liquid NH_3 at —60°, yielding $CHMe$:$CH·CH(OH)·C$:CH (**I**) (46%), b.p. 66°/20 mm., *γ-methyl-*Δ$^{\delta}$*-penten-*Δ$^{\alpha}$*-inen-γ-ol* (21%), b.p. 58—59°/60 mm., *γ-methyl-* (27%), b.p. 61—62°/25 mm., and *γε-dimethyl-*Δ$^{\delta}$*-n-hexen-*Δ$^{\alpha}$*-inen-γ-ol* (24%), b.p. 65—66°/17 mm., and *ε-phenyl-γ-methyl-*Δ$^{\delta}$*-penten-*Δ$^{\alpha}$*-inen-γ-ol* (20%), m.p. 50—51°, b.p. 114—116°/4 mm. With HgO and a little BF_3 in MeOH, (**I**) gives 2 : 5-*dimethoxy*-2 : 5-*dimethyl*-3 : 6-*dipropenyl*-1 : 4-*dioxan* (22%), m.p. 119—120°. *n* and *d* for the products are recorded. R. S. C.

[Ethylene] glycol complexes of the light transition metals. R. Gomer and G. N. Tyson, jun. (*J. Amer. Chem. Soc.*, 1944, **66**, 1331—1333).—The under-mentioned *compounds* of metal salts with $(CH_2·OH)_2$ (**I**) are prepared. Magnetic data, which are recorded, show that all are ionic. Colours of Co^{II} compounds are independent of the geometric form. The no. of unpaired electrons is indicated by *UE* below. $CuSO_4$,(**I**) and $CuSO_4$,2(**I**), light blue (*UE* 1); $FeSO_4$,(**I**), +2H_2O, light yellow (*UE* 4); *X*,2(**I**), +H_2O, where *X* = $NiSO_4$, light green (*UE* 2), $CoCl_2$, dark blue (*UE* 3), or $MnCl_2$, pale rose (*UE* 5); $FeSO_4$,3(**I**), light yellow (*UE* 4); $CoCl_2$,3(**I**), dark blue; *X*,3(**I**), +H_2O, where *X* = $NiSO_4$, light green (*UE* 2), $CoCl_2$, pink (*UE* 3), or $FeSO_4$, yellowish-green; $NiSO_4$,4(**I**), light green (*UE* 2). R. S. C.

Halogen derivatives of cineole.—See A., 1944, II, 374.

Dihydroxypropyl bismuthate, m.p. 240—245° (decomp.).—See A., 1944, III, 684.

αγ: βδ-Dimethylene- and βδ-methylene-*D-epi*rhamnitol. A. T. Ness, R. M. Hann, and C. S. Hudson (*J. Amer. Chem. Soc.*, 1941, **66**, 1235—1237).—αγ : βδ-Dimethylene-*D*-sorbitol with *p*-$C_6H_4Me·SO_3H$ in C_5H_5N at 0° and later 23° gives the ζ-p-*toluenesulphonate* (82%), m.p. 160—161°, $[\alpha]_D$ −10·0° in $CHCl_3$, converted by NaI in, best (90%), $COMe_2$ at 100° into the ζ-*iodide*, m.p. 177—179°, $[\alpha]_D^{20}$ −21·7° in $CHCl_3$, whence H_2–Raney Ni in aq. NaOH at slightly >1 atm. gives αγ : βδ-*dimethylene*-D-epi*rhamnitol* (**I**) (89%), m.p. 182—183°, $[\alpha]_D^{20}$ −40·9° in H_2O. *D-epi*Rhamnitol (prep. from methyl-β-*D-ebi*rhamnoside), conc. HCl, and 37% CH_2O at room temp. (4 days) over NaOH–H_2SO_4 give (**I**), $[\alpha]_D^0$ −40·6° in H_2O. Ac_2O–

AcOH–H_2SO_4 at 0° converts (I) into *γ-acetoxymethyl-ββδ-methylene*-D-epi*rhamnitol* αε-*diacetate* (87%), m.p. 116—117°, $[\alpha]_D^{20}$ +5·3° in $CHCl_3$, converted by NaOMe–$CHCl_3$–MeOH into *ββδ-methylene*-D-epi-*rhamnitol* (100%), m.p. 176—177°, $[\alpha]_D^{20}$ −20·2° in H_2O, which is stable to aq. HIO_4 at 25° and in Ac_2O–C_5H_5N at 25° (3 days) yields the *αγε-triacetate*, m.p. 149—150°, $[\alpha]_D^0$ −0·6° in $CHCl_3$, −1·8° in $COMe_2$. Structures are proved by the reactions described. M.p. are corr. R. S. C.

Carbohydrate *C*-nitro-alcohols. α-Nitro-α-deoxy-*D*-mannitol. J. C. Sowden and H. O. L. Fischer (*J. Amer. Chem. Soc.*, 1944, **66**, 1312—1314).—4 : 6-Benzylideneglucose with NH_2OH–EtOH at 70° gives the *oxime* (83%), m.p. 195° (decomp.), $[\alpha]_D^{27}$ −72° in C_5H_5N, converted by Ac_2O–NaOAc at 120—125° into 4 : 6-*benzylidenegluconitrile* 2 : 3 : 5-*triacetate*, m.p. 135·5—136°, $[\alpha]_D^{25}$ +44° in $CHCl_3$, which with $MeNO_2$ and NaOMe in MeOH at ~5° (42 hr.) yields *α-nitro-δζ-benzylidene-α-deoxy*-D-*mannitol* (I) (31%), m.p. 146—147°, $[\alpha]_D^{21}$ −70·4° in H_2O (cf. Pictet *et al.*, A., 1922, i, 4), the corresponding sorbitol derivative being sol. In 0·1N-H_2SO_4 at 70° (I) gives *α-nitro-α-deoxy*-D-*mannitol* (78%), m.p. 134·5—135°, $[\alpha]_D$ −7·0° in H_2O, which gives a red colour in the Griess–Ilosvay test and reduces hot Fehling's solution. H_2–Raney Ni reduces (I) at room temp. to α-amino-δζ-benzylidene-α-deoxymannitol [*oxalate*, m.p. 208° (decomp.), $[\alpha]_D^0$ −37° in H_2O], whence dil. H_2SO_4 at 70° yields α-amino-α-deoxymannitol [oxalate, m.p. 183—184° (decomp.), $[\alpha]_D$ +5·0° in H_2O]. ~8% H_2SO_4 at 35—40° converts (I) into mannose, which is isolated as phenyl- or phenyl-α-methyl-hydrazone. R. S. C.

Peroxidation of ethyl ether. R. Viallard (*Bull. Soc. chim.*, 1943, [v], **10**, 512—516).—Analysis of the products formed from Et_2O and O_3 indicates the formation of dihydroperoxydiethyl oxide ozonide (I) and $O_3{:}O(CHMe{\cdot}O_2H)_2$; (I) would yield MeCHO thus: $O_3{:}O(CHMe{\cdot}O_2H)_2 \rightarrow OH{\cdot}O(O_3){\cdot}CHMe{\cdot}O_2H + MeCHO$. A. T. P.

[Oxidation of di*iso*propyl ether.] G. Wittig (*Ber.*, 1942, **75**, [*B*], 1301).—In reply to the statement that "monomeric ketone peroxides" have not yet been discovered (Rieche *et al.*, A., 1943, II, 79) it is pointed out that monomeric fluorenone peroxide has been described by Wittig *et al.* (A., 1942, II, 49). H. W.

Acetyl phosphate: chemistry, determination, and synthesis. F. Lipmann and L. C. Tuttle (*J. Biol. Chem.*, 1944, **153**, 571—582).—The synthesis of AcH_2PO_4 (I) (cf. Lynen, A., 1943, II, 250) is simplified. $Ag_3PO_4 + 2H_3PO_4$ and AcCl–Et_2O give a product which is treated with aq. Na_2CO_3 (to pH 3—3·5); AcOH is removed by Et_2O, aq. NaOH added (to pH 7), and Na_2PO_4 frozen out and filtered off from (I) at ≯ −5°. The Ag_2 salt is prepared (cf. *loc. cit.*), and similarly the Ag_2 salts $COEt{\cdot}O{\cdot}PO(OAg)_2$ and $COPr{\cdot}O{\cdot}PO(OAg)_2$. From $(CH_2{\cdot}COCl)_2$ and Ag_3PO_4–H_3PO_4 [removing $(CH_2{\cdot}CO_2H)_2$ by EtOAc], a mixture of succinyl phosphate (40%) and diphosphate (60%) is similarly obtained. The rate of decomp. of (I) is studied under various conditions. Max. stability is at pH 5—6. The hydrolysis of (I) by 0·0N-HCl is very greatly accelerated by $(NH_4)_6Mo_7O_{24}$; rates are identical for (I) prepared as above or from $AcCO_2H$ and *B. delbrückii* (cf. A., 1940, II, 266). Methods of determining (I), depending on MoO_4'' colorimetry and on the solubility of $AcCaPO_4$ are described (cf. C., 1945, Part 1). E. W. W.

Inhibition of catalysed oxidations by hæmins.—See A., 1944, III, 838.

Preparation of glucose 1-phosphate. J. B. Sumner and G. F. Somers (*Arch. Biochem.*, 1944, **4**, 11—13).—A modification of the procedure of Green and Stumpf (A., 1942, III, 419), in which a preliminary digestion of dextrins with pancreatic amylase is introduced, is given. E. R. S.

Action of ozone on thioethers. H. Bohme and Harriet Fischer (*Ber.*, 1942, **75**, [*B*], 1310—1311).—The sulphide, dissolved in abs. $CHCl_3$, is saturated with O_2–O_3 at 0° and the solvent is removed in vac. at room temp. or 0°. Thus are obtained: Me_2SO_2, Et_2SO_2, $(Cl{\cdot}[CH_2]_2)_2SO_2$, $PhMeSO_2$, $CH_2Ph{\cdot}SO_2Et$, and $(CH_2Ph)_2SO_2$. The isolation of $(CH_2Ph)_2SO$ by use of an insufficiency of O_3 indicates the intermediate production of sulphoxides. *CH_2Cl Et sulphoxide* has b.p. 70°/0·2 mm. H. W.

New synthesis of β-keto-esters of the type, COR·CH_2·CO_2Et. D. S. Breslow, E. Baumgarten, and C. R. Hauser (*J. Amer. Chem. Soc.*, 1944, **66**, 1286—1288).—Treating $CO_2Et{\cdot}CH_2{\cdot}CO_2Bu^\gamma$ (I) with Mg turnings and a little CCl_4 in boiling EtOH or with $Mg(OEt)_2$–Et_2O and then RCOCl gives $COR{\cdot}CH(CO_2Et){\cdot}CO_2Bu^\gamma$, which with a little *p*-$C_6H_4Me{\cdot}SO_3H$ in boiling C_6H_6 gives $CMe_2{:}CH_2$ and $COR{\cdot}CH_2{\cdot}CO_2Et$ (cf. A., 1944, II, 320). Decomp. of $CHBz(CO_2Et)_2$ in steam gives only a poor yield of $CH_2Bz{\cdot}CO_2Et$ (cf. Bernhard, A., 1895, i, 93) and the method is not well applicable to aliphatic compounds. Prep. of (I) in 48—55% yield from $CH_2(CO_2Et)_2$ is described. The synthesis is applied to yield $COEt{\cdot}CH_2{\cdot}CO_2Et$ (63%), Et β-keto-β-*cyclo*hexyl- (65%), b.p. 146—150°/18 mm., and -β-2-furyl-propionate (70%), b.p. 137—139°/9·5 mm., $CH_2Ph{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et$ (47%), b.p. 154—156°/9 mm., and $CHMe{:}CH{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et$ (35%), b.p. 101—105°/15 mm. (*Cu* salt, m.p. 159°). $CHBu^\alpha(CO_2Et)_2$ yields $CO_2Et{\cdot}CHBu^\alpha{\cdot}COCl$, b.p. 90—107°/9·5 mm., and thence $CO_2Et{\cdot}CHBu^\alpha{\cdot}CO_2Bu^\gamma$, b.p. 126—128°/15 mm., which, as above, gives *Et α-benzoyl-n-hexoate*, b.p. 157—161°/5 mm. (derived *amide*, m.p. 153—154°). R. S. C.

Synthesis, some derivatives, and metabolism of αβ-diketo-octoic acid.—See A., 1944, II, 379.

Autoxidation of oxygen-active acids. VII. Action of molecular oxygen on methyl licanate. W. Treibs (*Ber.*, 1942, **75**, [*B*], 1373—1376).—The conjugated triene system of Me licanate [γ-keto-$\Delta^{\theta\kappa\mu}$-octatrienoate] (I) is responsible for the reaction between the ester and mol. O_2 whereas the CO group takes no direct part but merely acts as an accelerating catalyst. The course of the reaction is identical with that of clæostearic esters. (I) boils unchanged at 240—242°/20 mm. but after long heating at 280° shows signs of incipient cyclisation and simultaneous dimerisation. It can be kept unchanged for months at 20° in sealed vessels under N_2. The viscosity of (I) increases very greatly after absorption of a little O_2, showing immediate mol. enlargement. The absorption of O_2 by (I) and Me clæostearate (II) when spread on glass plates is found gravimetrically to be closely similar and different from that of esters with isolated double linkings. The autoxidative similarity of (I) and (II) is shown particularly by the alteration of *n* and *d* in the products. Similar results are obtained by periodic examination of the autoxidation products with MeMeI. Licanic acid and boiling Ac_2O give a polyfunctional material as a dry, very hard film in place of the expected acetate. H. W.

Production of succinic acid.—See B., 1944, II, 303.

Synthesis of α-bromo-aldehydes. P. Z. Bedoukian (*J. Amer. Chem. Soc.*, 1944, **66**, 1325—1327).—Converting aldehydes by boiling Ac_2O–KOAc into the enol acetates (35—80%) and adding to these in CCl_4 Br (1 mol.) and then an excess of MeOH gives $CHRBr{\cdot}CH(OMe)_2$ (75—80%), which are stable when pure but are very sensitive to acidic impurities and in hot acid (HCl or 50% citric acid) give 25—95% of CHRBr·CHO. Thus are obtained the enol *acetates* of PrβCHO, b.p. 124—126°, *n*-C_6H_{13}·CHO, b.p. 88—90°/17 mm., and PhCHO, b.p. 113—115°/10 mm., $CMe_2Br{\cdot}CHO$, b.p. 113—115° (2 : 4-*dinitrophenyldrazone*, m.p. 116°; Me_2 acetal, b.p. 5°—54°/10 mm.), *n*-$C_5H_{11}{\cdot}CHBr{\cdot}CHO$, b.p. 90°/17 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 106°; *Me_2 acetal*, b.p. 117—119°/17 mm.), and *α-bromophenylacetaldehyde*, b.p. 108—109°/10 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 139°; *Me_2 acetal*, b.p. 133—135°/10 mm.).

Action of ammonia on crotonaldehyde.—See A., 1944, II, 380.

Preparation of unsaturated ketones.—See B., 1944, II, 303.

Triacetone dialcohol and its dehydration products. E. E. Connolly (*J.C.S.*, 1944, 338—339).—The vac.-still residues from large-scale production of diacetone alcohol (I) contain s-*triacetone dialcohol* (*βζ-dimethylheptane-βζ-diol-δ-one*) (II) (cf. Leopold *et al.*, G.P. 481,290), m.p. 56·4°, b.p. 128°/15 mm. When distilled with syrupy H_3PO_4, (II) gives "semiphorone" (*βζ*-dimethyl-Δ^ϵ-hepten-β-ol-δ-one) (III) (cf. Grignard *et al.*, A., 1929, 396). When heated with a little conc. H_2SO_4, (II) gives phorone (IV) [H_2O which is also formed is carried away by $CHAc{:}CMe_2$ (V) derived from $CH_2Ac{\cdot}CMe_2{\cdot}OH$ in crude (II), or by excess of C_6H_6, which is added when cryst. (II) is used]. Cryst. (II) when heated under reflux with dil. H_2SO_4 gives (IV), 2 : 2 : 6 : 6-*tetramethyltetrahydro*-1 : 4-*pyrone* (VI), m.p. 12·8°, b.p. 70°/15 mm. (oxime, m.p. 101°), and (III). (VI) is dehydrated to (IV). With 2 : 4 : 1-$C_6H_3(NO_2)_2{\cdot}NH{\cdot}NH_2$, (I) and (V) give the same product, m.p. 197—198°, whilst (II), (III), and (VI) give a second product, m.p. 171—173°, different from that, m.p. 118—188·5°, obtained from (IV). E. W. W.

Reductone and vitamin-*C*. J. G. A. Griffiths (*Nature*, 1943, **152**, 163).—$(CHO)_2$ may be obtained from O_3, H_2O, and C_2H_2, and reductone from $(CHO)_2$, by irradiation with ultra-violet light. E. R. R.

New reagent for primary and *sec.* amines.—See A., 1944, II, 372.

Complex compounds of cupric azide. III. Non-electrolytes with organic bases.—See A., 1944, I, 290.

Preparation, resolution, and optical properties of β-amino-*n*-octane. F. G. Mann and J. W. G. Porter (*J.C.S.*, 1944, 456—461).—CrO_3 oxidation of *n*-octan-β-ol gives ~95% yield of $COMe{\cdot}C_6H_{13}$-*n*, the oxime of which is reduced with Na and EtOH to pure β-amino-*n*-octane in 70% yield (*Bz* derivative, m.p. 73—74°; *hydrochloride*, m.p. 91—92°; *phenylhydrazone*, b.p. 119—120°/0·05 mm.). The *l*-amine is prepared by repeated recrystallisation of the *dl*-amine H *d*-tartrate from MeOH; similarly the H *l*-tartrate gives the *d*-amine. The rotations of the pure amine and its C_5H_5 solution are similar and that of the EtOH solution, which is unaffected by the concn. The d- and l-*amine hydrochlorides*, m.p. 90—91°, are freely sol. in ionising and in non-ionising solvents, in which they are associated. They show a pronounced "acid effect," *e.g.*, the *l*-amine hydrochloride gives strongly dextrorotatory solutions in ionising solvents, *e.g.*, H_2O, MeOH, EtOH, $HCO{\cdot}NH_2$, the rotation in EtOH being almost independent of concn.; in non-ionising solvents, as the concn. is progressively increased, the lævorotation decreases to zero, *e.g.*, in PhMe or dioxan saturated at room temp., and becomes a dextrorotation at moderately high concns., *e.g.*, in CH_2Cl_2, $C_2H_4Cl_2$, $CHCl_3$, C_6H_6. The d-*camphorsulphonate*, m.p.

162—165°, $[M]_D^{19}$ +49·5°, and d-α-*bromocamphorsulphonate*, m.p. 180—185°, of the *dl*-amine are unsuitable for resolution. H. D. W.

Production of β-aminopropionic acid.—See B., 1944, II, 303.

Hydroxyleucines. H. D. Dakin (*J. Biol. Chem.*, 1944, **154**, 549—555).—*iso*Butene oxide (excess) and NHAc·CH(CO_2Et)$_2$ in dioxan with NaOMe, followed by hydrolysis (HCl), give *γ-hydroxyleucine* (I), m.p. 226—228°, purified through the *flavianate*, m.p. 272—273°. (I) is apparently not identical with the small amount of NH_2-acid, $C_6H_{13}NO_3$, m.p. 248—250°, obtained from casein. *Glycine flavianate* has m.p. 244—245° (efferv.). F. R. S.

ε-Diethylaminoamyl β-dithiocarbamate, m.p. 136—138°.—See C., 1944, 167.

Preparation of nitrourea.—See B., 1944, II, 304.

Manufacture of cyanohydrins.—See B., 1944, II, 304.

Ethylenic nitriles; Δ^α- and Δ^β-octenonitrile. R. Delaby and J. Hubert (*Bull. Soc. chim.*, 1943, [v], **10**, 576—580).—CHBu^α:CH·CH_2Br (I) or mixtures of (I) and CHBu^{α}Br·CH:CH_2, heated slowly with CuCN to 100—105°, then at 100° for 1 hr., give trans-Δ^β-*octenonitrile* (II), b.p. 93—95°/20 mm., and some Δ^α-*octenonitrile*. Raman spectra of the various fractions are examined. Hydrogenation (Raney Ni–EtOH) of (II) gives C_8H_{17}·NH_2. (II) is transformed into cis-, b.p. 78—80°/15 mm. and trans-Δ^α-*octenonitrile* (III), b.p. 88—90°/15 mm. by adding to PhOH–Na_2CO_3 (previously heated at 150°) at 150° for 2 hr. HCl is introduced into (II) or (III) (mixture of *cis-* and *trans-*) and SH·CH_2·CO_2H in Et_2O for 5 hr. (method: Condo *et al.*, A., 1937, II, 139) to yield 40—50% of the respective *adduct*, *e.g.*, RCN CO_2H·CH_2·S·CR:NH,HCl. The reaction is much more rapid in the cases of CHMe:CH·CN and CH_2:CH·CH_2·CN. With such nitriles, fixation of Br is the slower the greater is the mol. wt. A. T. P.

II.—SUGARS AND GLUCOSIDES.

Existence and significance of sugar–triose equilibrium. C. Enders and S. Sigurdsson (*Naturwiss.*, 1943, **31**, 92—93).—Determinations of the AcCHO contents of distillates from 0·2 and 2·0% solutions of sugars are used as basis for calculating the consts. of the thermodynamic equilibria which exist between sucrose (I), maltose, galactose, mannose, glucose, fructose (II), arabinose, and xylose, on the one hand, and the primary product of hydrolysis, a triose which readily (*e.g.*, by heating) changes into AcCHO. The vals. obtained form a series decreasing in the order named, from (I) to (II), the position of the equilibria being dependent on temp., pH, and the nature of any acid present. The existence of the triose, which is possibly a hydrated form of glyceraldehyde, provides an explanation of many problems of carbohydrate chemistry. W. McC.

Analysis of mixtures of 2 : 3 : 4 : 6-tetramethylglucose with 2 : 3 : 6-trimethyl- and dimethyl-glucoses by partition on a silica water column : small-scale method for investigating structures of glucopolysaccharides. D. J. Bell (*J.C.S.*, 1944, 473—476).—Abs. separation of 50—200 mg. of 2 : 3 : 4 : 6-tetramethyl- from 2 : 3 : 6-trimethyl-glucose (I) (1—200 mols.) and dimethylglucoses is achieved by partition of a $CHCl_3$ extract of the aq. solution on a SiO_2–H_2O column; further extraction of the aq. solution with $CHCl_3$–BuOH (9 : 1) and partition of the extract on the same column gives (I) free from dimethylglucoses, which can be eluted with $COMe_2$. High recoveries of analytically pure sugars are obtained in both separations. The method is applied to determine the average length of unit chain in methylated derivatives of cellobiose, glycogen, and whole starch. H. D. W.

Enzymically synthesised crystalline sucrose. W. Z. Hassid, M. Doudoroff, and H. A. Barker (*J. Amer. Chem. Soc.*, 1944, **66**, 1416—1419).—The phosphorylase, freed from invertase, of *Pseudomonas saccharophila* is kept with K glucose 1-phosphate, fructose, and $Ba(OAc)_2$ in H_2O at 37° and pH 6·85 for 12 hr. and then at 29° for a further 12 hr. Cooling, filtration, removal of electrolytes by chromatography and of monosaccharides by washed cells of *Torula monosa*, concn., and treatment with EtOH gives sucrose, $[\alpha]_D$ +66·5° in H_2O (cf. Doudoroff *et al.*, A., 1943, III, 599; 1944, III, 88), identified by its osazone, *X*-ray spectrum, crystallo-optical properties, hydrolysis, and by its octa-acetate, m.p. 69—70°, $[\alpha]_D$ +60° in $CHCl_3$. The synthesis supports the view that glucose exists in sucrose in the α-form. R. S. C.

Separation of methylated methylglycosides by adsorption on alumina. New method for end-group determinations in methylated polysaccharides. J. K. N. Jones (*J.C.S.*, 1944, 333—334).—Tetramethylmethylglucoside (I), mixed with excess of trimethylmethylglucoside, in Et_2O–light petroleum (also used for elution) is separated (44%) chromatographically on activated Al_2O_3, which also effects some separation between the α- and (less strongly adsorbed) β-forms. Rice starch (II) (Hirst *et al.*, A., 1939, II, 495) treated with MeOH–HCl and Ag_2CO_3 and chromatographed gives (I) and trimethyl-β-methylglucoside; the proportion of (I) in the mixed methylglucosides obtained indicates that there are 33 glucose residues in the repeating unit of (II). Banana starch (Hawkins *et al.*, A., 1940, II, 207), similarly treated, gives (I) in proportion indicating 26 residues per unit (cf *loc. cit.*), with trimethyl-β-methylglucopyranoside. Methylated damson gum hydrolysed by MeOH–HCl gives a mixture of glucosides containing a const.-boiling mixture separated chromatographically into fractions which are hydrolysed by 0·5N-HCl to 2 : 3 : 4-trimethyl-*d*-xylose and 2 : 3 : 5-trimethyl-*l*-arabofuranose; it thus contains trimethylmethyl-1-arabofuranoside and -*d*-xylopyranoside. E. W. W.

Preparation of *N*-*d*-ribityl-*o*-4-xylidine. M. Tishler, N. L. Wendler, K. Ladenburg, and J. W. Wellman (*J. Amer. Chem. Soc.*, 1944, **66**, 1328—1330).—*d*-Ribolactone, *o*-4-xylidine (I), and a trace of quinol at 100° give d-*ribono*-o-4-*xylidide*, m.p. 164—165° (slight decomp.), converted by Ac_2O–C_5H_5N at >45° into the *tetra-acetate* (II), m.p. 114—115°, $[\alpha]_D$ +16±1° in $CHCl_3$, whence PCl_5 in $CHCl_3$ at room temp. yields the *chloro-imide tetra-acetate* (III), m.p. 68—70° [reconverted into (II) by H_2O]. H_2–Pd–$BaCO_3$ or –$CaCO_3$ in EtOAc or dioxan at 50—55°/15—30 lb. reduces (III) to N-d-*ribityl*-o-4-*xylidine tetra-acetate*, m.p. 94—95° (cf. B.P. 550,169, 551,491; B., 1943, II, 107, 172), also obtained (m.p. 99—100°) by hydrogenating (Pd–C) *d*-ribonitrile tetra-acetate and (I) in MeOH–AcOH–H_2O at 5—10 lb. and hydrolysed by $Ba(OMe)_2$ or NaOMe in boiling MeOH to *N*-*d*-ribityl-*o*-4-xylidine, m.p. 142—143°. R. S. C.

Synthesis of asebotin. G. Zemplén and L. Mester (*Ber.*, 1942, **75**, [*B*], 1298—1301).—Phloracetophenone 4-Me ether and acetobromoglucose in aq. $COMe_2$ containing a small amount of NaOH give 2-*glucosidophloracetophenone 4-Me ether tetra-acetate*, m.p. 187·5°, $[\alpha]_D^{25}$ −46·3° in C_5H_5N, which is condensed with *p*-OH·C_6H_4·CHO by conc. KOH to 2-glucosidonaringenin 4′-Me ether. This is hydrogenated (Pd–C in 96% EtOH) to asebotin, m.p. 148° after softening, $[\alpha]_D^3$ −52·1° in 55% EtOH, −46·2° in abs. EtOH, hydrolysed by 2·5% HCl at 100° to phloretin 4′-Me ether, m.p. 158° and 167·5° (triacetate, m.p. 78—79°, softens at 76°). H. W.

Glucosides of 4-hydroxycoumarins.—See A., 1944, II, 345.

Gum tragacanth. S. P. James and F. Smith (*Biochem. J.*, 1944, **38**, *Proc.*, xix).—Gum tragacanth consists of tragacanthic acid, a neutral polysaccharide, and a sterol glucoside. Hydrolysis of methylated tragacanthic acid with MeOH–HCl yields 2 : 3 : 4-trimethyl-α-methyl-*l*-fucoside, 2 : 3 : 4-trimethyl-, and 3 : 4-dimethyl-methyl-*d*-xyloside, Me ester of 2 : 3-dimethylmethylgalactofuronoside, and methyl-β-methylgalactopyranoside. The acid is essentially a chain of galacturonic acid residues joined by 1 : 4-α linkings. Hydrolysis of the methylated polysaccharide by MeOH–HCl yields 2 : 3 : 5-trimethylmethyl-*l*-arabofuranoside; 2 : 3-dimethylmethyl-*l*-arabopyranoside, β-methyl-*l*-arabopyranoside, and a dimethylhexoside. The ease of hydrolysis and the high negative val. of [α] indicate the presence of arabinose units of the furanose type in the polysaccharide, which, however, is not a simple araban. P. G. M.

Water-soluble mannan from seeds of *Daubentonia drummondii*.—See A., 1944, III, 856.

III.—HOMOCYCLIC.

Preparation of benzene by Kolbe's synthesis. Electrolysis of *trans*-1 : 2-dihydrophthalic acid. E. A. Pasquinelli (*Anal. Asoc. Quím. Argentina*, 1943, **31**, 181—190).—Electrolysis (10 v., 5 amp.) of *trans*-1 : 2-dihydrophthalic acid yields C_6H_6. F. R. G.

Nitration of toluene. Continuous partial-pressure process using nitric acid alone.—See B., 1944, II, 301.

Nitrations with nitryl chloride.—See A., 1944, II, 357.

Hydrogen chloride as a condensing agent. J. H. Simons and H. Hart (*J. Amer. Chem. Soc.*, 1944, **66**, 1309—1312).—Anhyd. HCl resembles HF as catalyst for alkylation of aromatic hydrocarbons; it yields only *p*-compounds. PhMe with Bu^{γ}Cl, Pr^{β}Cl, or Bu^{α}Cl and HCl at 235°/200 atm. (apparatus: C, 1944, 197) gives *p*-C_6H_4MeBu^γ (88%), *p*-C_6H_4MePr^β (67%) + C_6H_3MePr$^β_2$ (16%), and *p*-C_6H_4MeBu^α (15%), respectively. C_6H_6 yields similarly at 150° PhBu^γ (45·5%) + *p*-C_6H_4Bu$^γ_2$ (24%), at 235° PhPr^β (48%) + *p*-C_6H_4Pr$^β_2$ (44%), and at 195° PhBu^α (30%) + *p*-C_6H_4Bu$^α_2$ (60%). C_6H_6, *cyclo*hexene (I), and HCl at 208° give *cyclo*hexylbenzene (37%), *cyclo*hexyl chloride (II) (27%), and some polymer. C_6H_6, AcCl, and HCl give no COPhMe, but BzCl at 200° leads to 4·4% of $COPh_2$. PhBu^γ, PhOH, and HCl do not give C_6H_6 + *p*-C_6H_4Bu^γ·OH (III). PhOH, Bu^{γ}Cl, and HCl at 75°/200 atm. give 90% of (II) but 67% is obtained by merely boiling PhOH and Bu^{γ}Cl without a catalyst; catalytic effect of HCl in the general reaction is shown by failure of PhMe and Bu^{γ}Cl to condense at 235°/575 lb. (N_2). PhOH, *tert.*-C_5H_{11}Cl, and HCl at 90—160° give 72% of *p*-*tert.*-C_5H_{11}·C_6H_4·OH. *iso*-C_5H_{12}, (I), and HCl at 200—220° give 30% of (II), 40% of polymer, and 4% of a saturated hydrocarbon, b.p. 195—200°. R. S. C.

Catalytic aromatisation of branched-chain aliphatic hydrocarbons.—See A., 1944, II, 357.

Thermal polymerisation and cyclic dimerisation of *iso*butylene.—See A., 1944, II, 357.

Synthesis of polyenes. IV. M. S. Kharasch, W. Nudenberg, and E. K. Fields (*J. Amer. Chem. Soc.*, 1944, **66**, 1276—1279; cf. A., 1943, II, 159).—Condensation of CH_2RHal by $NaNH_2$ in liquid NH_3 to $(CHR:)_2$ proceeds by way of $CH_2R{\cdot}CHRHal$ and depends on R being strongly electronegative and not containing reactive substituents and on the high dielectric const. of the solvent. A detailed reaction mechanism is propounded. $CH_2Ph{\cdot}NH_2,HCl$ (5%) is obtained from CH_2PhCl by KOH, NaOEt, or $CHO{\cdot}NHNa$ in liquid NH_3, or (15%) by $NaNH_2$ in Et_2O; $CHO{\cdot}NHNa$ in $HCO{\cdot}NH_2$ gives $CHO{\cdot}N(CH_2Ph)_2$ (55%); $NaNH_2$ in light petroleum is without effect, but in liquid NH_3 gives 100% of $(CHPh:)_2$. With $NaNH_2$ in liquid NH_3, CH_2BzBr gives $(CHBz:)_2$ (42%), m.p. 111°; $(CH_2Br{\cdot}CH:)_2$ gives a *polymer*, $CH_2Br{\cdot}[CH:CH]_x{\cdot}CH_2Br$ (100%); $CHPh:CH{\cdot}CH_2Cl$ gives *αζ-diphenylhexatriene* (10%), *form*, softens 150—160°, m.p. 165°, but an excess of $NaNH_2$ leads to polymeric products; $(o\text{-}CH_2Br{\cdot}C_6H_4)_2$ gives 80% of phenanthrene; $CH_2PhCl + CH_2{:}CH{\cdot}CH_2Cl$ gives $CHPh:CH{\cdot}CH:CH_2$ (14%), styrene, hexatriene, and polymers; $CH_2PhCl + CH_2{:}CMe{\cdot}CH_2Cl$ gives $CHPh:CMe{\cdot}CH:CH_2$ (23%), styrene (13%), $(CH_2{:}CMe{\cdot}CH:)_2$ (35%), and polymers (29%); geranyl chloride gives 35% of geranylamine. 6-*Phenyl*-4-*methyl*-, m.p. 194° (decomp.) (*anhydride*, m.p. 90—91°), and 6-*phenyl*-, m.p. 200—203° (decomp.; rapid heating), -1 : 2 : 3 : 6-*tetrahydrophthalic acid* are prepared. R. S. C.

Preparation of substituted styrenes. L. A. Brooks (*J. Amer. Chem. Soc.*, 1944, **66**, 1295—1297).—*o*-$C_6H_4Cl{\cdot}CHO$ with $MgMeBr$–Et_2O gives α-o-*chlorophenylethyl alcohol* (76%), b.p. 109°/7 mm., converted by >1% of $KHSO_4$ and a little quinol at 200—210°/110—130 mm. into o-*chlorostyrene* (70%), b.p. 60—61°/4 mm. Similarly are prepared α-m-, b.p. 102—104°/3 mm., and α-p-*chlorophenyl*-, b.p. 87—89°/2 mm., α-o-, b.p. 117—118°/45 mm., α-m-, b.p. 120—121°/45 mm., and α-p-*fluorophenyl*-, b.p. 122—123°/45 mm., and α-2 : 5-*dichlorophenyl-ethyl alcohol*, m.p. 63—64°, b.p. 107—109°/2 mm., and thence *m*-, b.p. 62—63°/6 mm., and *p*-chloro-, b.p. 53—54°/3 mm., o-, b.p. 32—34°/3 mm., m-, b.p. 30—31°/4 mm., and p-*fluoro*-, b.p. 29—30°/4 mm., and 3 : 5-*dichloro-styrene*, b.p. 72—73°/2 mm. 3 : 4 : 1-$C_6H_3Cl_2{\cdot}COMe$ yields α-3 : 4-*dichlorophenylethyl alcohol* (91%), b.p. 127—128°/2 mm., and thence 3 : 4-*dichlorostyrene*, b.p. 69—70°/4 mm. The styrenes are less stable when purified. Relative stabilities of $CHAr{:}CH_2$ are $Ar = C_6H_4F > C_6H_4Cl > C_6H_3Cl_2$. R. S. C.

Reactivity of 2-chloro-3 : 5-dinitrodiphenyl. C. K. Bradsher and S. T. Amore (*J. Amer. Chem. Soc.*, 1944, **66**, 1283—1284).—1 : 2 : 3 : 5-$C_6H_2PhCl(NO_2)_2$ (**I**), best obtained (m.p. 115—116°; cf. Borsche *et al.*, A., 1917, i, 390) from 3 : 5 : 1 : 2-$(NO_2)_2C_6H_2Ph{\cdot}NH_2$ by $NO{\cdot}SO_3H$ and then aq. CuCl–HCl, differs from 1 : 2 : 4-$C_6H_3Cl(NO_2)_2$ owing to steric hindrance by the Ph. In boiling NaOR–ROH, (**I**) gives 3 : 5-*dinitro*-2-*ethoxy*- (**II**) (93%), m.p. 114—115°, and -2-methoxy-diphenyl, m.p. 113·5—114°, in boiling piperidine gives 3 : 5-*dinitro*-2-*piperidinodiphenyl*, m.p. 184·5—185°, and with Cu powder at 215° and then 190° gives 4 : 6 : 4′ : -*tetranitro*-2 : 2′-*diphenyldiphenyl*, m.p. 248—249°. $CH_2(CO_2Et)_2$ or $CH_2Ac{\cdot}CO_2Et$ does not react with (**I**); $CH_2(CO_2Et)_2$ in NaOEt–EtOH gives only (**II**). R. S. C.

Bond system and stereochemistry of cumulenes.—See A., 1944, I, 268.

Di*cyclo*hexadienes and the strain theory.—See A., 1944, I, 267.

Aromatic cyclodehydration. XVI. Phenanthrene hydrocarbons from unsymmetrical ketones. C. K. Bradsher and S. T. Amore. **XVII. 9- and 10-Methyl-1 : 2 : 3 : 4-dibenzphenanthrene.** C. K. Bradsher and L. Rapoport (*J. Amer. Chem. Soc.*, 1944, **66**, 1280, 1281—1282; cf. A., 1944, II, 130).—XVI. *o*-$C_6H_4Ph{\cdot}MgI$ with $COR{\cdot}CH_2R'$ and then $KHSO_4$ gives α-*phenyl*-α-2-*diphenylyl*-Δ$^{\alpha}$-n-*pentene* (65%), m.p. 78—79°, b.p. 207—208°/8 mm., and -Δ undecene (60%), b.p. 242—254°/5 mm., β-2-diphenyl-Δ$^{\beta}$-*n*-butene (36%), b.p. 132—140°/9 mm., and -Δ$^{\alpha}$-*n*-heptene (51%), b.p. 140—160°/8 mm., and thence by oxidation and cyclisation 9-*phenyl*-10-n-*propyl*- (64%), m.p. 148·5—149·5°, 9-*phenyl*-10-n-*decyl*- (39%), m.p. 99—100°, 9 : 10-dimethyl- (39%), m.p. 142·5—143° (lit. 139°) (picrate, m.p. 193—194°), and 9-*n*-amyl-phenanthrene (31%), m.p. 69—70°.

XVII. 1-Keto-4-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene and *o*-$C_6H_4Ph{\cdot}Li$ in boiling Et_2O give 4-2′-*diphenylyl*-1-*methyl*-1 : 2-*dihydronaphthalene* (64·5%), b.p. 215—218°/6—7 mm., converted by *o*-$CO_2H{\cdot}C_6H_4{\cdot}CO_3H$ and then HBr–AcOH–H_2O into 9-methyl-9 : 10-dihydro-1 : 2 : 3 : 4-dibenzphenanthrene (89·5%), an oil (*picrate*, m.p. 170·5—171°), whence 30% Pd–C in CO_2 at 310—350° yields 9-*methyl*-1 : 2 : 3 : 4-*dibenzphenanthrene* (**I**) (64%), m.p. 150·5—151·5° (*picrate*, m.p. 207·5—208·5°). $Na_2Cr_2O_7$–AcOH oxidises (**I**) to 1 : 2 : 3 : 4-dibenzphenanthraquinone (proof of structure). (**I**) absorbs O_2 fairly rapidly in air. 1-Keto-3-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene leads similarly to 4-2′-*diphenylyl*-2-*methyl*-1 : 2-*dihydronaphthalene* (65%), m.p. 77—78°, 10-*methyl*-9 : 10-*dihydro*- (73%), m.p. 151—152° [unstable picrate, m.p. 117·5—119°; *s*-$C_6H_3(NO_2)_3$ *compound*, m.p. 138·5—139·5° after softening], and 1 *methyl*-1 : 2 : 3 : 4-*dibenzphenanthrene* (70%), m.p. 163·5—164° [unstable picrate, m.p. 150·5—151·5°; *s*-$C_6H_3(NO_2)_3$ *compound*, m.p. 161—162°]. 1-Keto-3 : 4-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene gives 4-2′-*diphenylyl*-1 : 2-*dimethyl*-1 : 2-*dihydronaphthalene*, m.p. 78—79·5°, b.p. 217—218°/8 mm., and 9 : 10-dimethyl-9 : 10-dihydro-1 : 2 : 3 : 4-dibenzphenanthrene, a resin (picrate, m.p. 154—154·5°), which is unchanged by chloranil and with Pd–C–CO_2 at 310—350° or S at 250° yields only (**I**). R. S. C.

Aromatic hydrocarbons. XXXIV. New synthesis of hexacene. E. Clar (*Ber.*, 1942, **75**, [*B*], 1283—1287; cf. A., 1940, II, 75).—*o*-$C_6H_4(CO)_2O$ is condensed with *o*-xylene to *o*-3 : 4-dimethylbenzoylbenzoic acid, which is oxidised by $KMnO_4$ in alkaline solution to benzophenone-2′ : 3 : 4-tricarboxylic acid. This passes at ~240° into the anhydride, m.p. 185—186° (lit. 175°), which is condensed with tetrahydronaphthalene by $AlCl_3$ in $C_2H_2Cl_4$ at 90° to *p*-*o*′-carboxybenzoyl-*o*-5 : 6 : 7 : 8-tetrahydro-2-naphthoylbenzoic acid, which could not be obtained cryst. It is reduced by Cu–Zn in alkaline solution to *p*-*o*′-carboxybenzyl-*o*-5 : 6 : 7 : 8-tetrahydronaphthyl-2-methylbenzoic acid, transformed by Zn dust, NaCl, and ZnCl, at 340° into a mixture from which 5 : 16-*dihydrohexacene* (**I**) is isolated by fractional sublimation in CO_2/1 mm. Its constitution is deduced from its orange-red colour, its absorption spectrum in C_6H_6, and great reactivity towards $(CH{\cdot}CO)_2O$. In boiling xylene (**I**) passes into 6 : 15-*dihydrohexacene* (**II**), which is pale yellow in colour, reacts more difficultly with $(CH{\cdot}CO)_2O$, and shows the absorption spectrum of a $C_{10}H_8$ and an anthracene complex united by 2 CH_2. (**I**) and (**II**) have m.p. 357—370° (vac.), ill-defined by reason of thermal transformability. Dehydrogenation of (**I**) or (**II**) gives hexacene. Pure (**II**) is oxidised in boiling $PhNO_2$ by SeO_2 to *hexacene*-6 : 15-*quinone*, m.p. (indef.) 295—310°, possibly containing the -5 : 16-isomeride. H. W.

Complex compounds of cupric azide. III. Non-electrolytes with organic bases.—See A., 1944, I, 290.

Photochemical investigation of dark-coloured aniline.—See A., 1944, I, 289.

Influence of alkyl groups on reaction velocities in solution. V. Formation of phenyltrialkylammonium iodides in methyl alcohol.—See A., 1944, I, 286.

Phenylthiocarbimide from phenyl azide. W. Borsche (*Ber.*, 1942, **75**, [*B*], 1312—1313).—PhN_3 and $AlCl_3$ in $PhNO_2$ give N_2 and a dark resin from which no definite compound could be isolated. In CS_2 the products are PhNCS and "phenylthiocarbimide sulphide," CS<S—S>C:NPh, m.p. 155°. The first products are therefore N_2 and PhN. H. W.

Preparation and properties of derivatives of sulphamide. K. W. Wheeler [with E. F. Degering] (*J. Amer. Chem. Soc.*, 1944, **66**, 1242—1243).—$SO_2(NH_2)_2$ and $CO_2H{\cdot}CH_2{\cdot}COCl$ in Et_2O give *H malonylsulphamide*, $CO_2H{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}SO_2{\cdot}NH_2$, m.p. 147° (decomp.; uncorr.), which in EtOH–H_2SO_4 gives (?) the Et ester, m.p. 84—85° (uncorr.). SO_2Cl_2 (2 mols.) and $NHMe_2$,HCl (1 mol.) at 60° give HCl and $NMe_2{\cdot}SO_2Cl$ (80%). $NAlk_2{\cdot}SO_2Cl$ with NH_2R or NHR_2 alone (exothermally) or in boiling C_6H_6 or Et_2O yields N-o-, m.p. 64·6—65·2°, and N-m-*tolyl*-, m.p. 47—48°, N-m-4-*xylyl*-, m.p. 74·7—75°, N-o-*chlorophenyl*-, m.p. 49·4—49·7°, and N-p-*anisyl*-, m.p. 56·3—56·8°, -N′N′-*diethylsulphamide*; N-*phenyl*-NN′N′-*trimethylsulphamide*, m.p. 45·5—46°, and -N′N′-*dimethyl*-N-*ethylsulphamide*, m.p. 31·5—32°; N-o-, m.p. 104·8—105·2°, and N-m-*tolyl*-, m.p. 80·5—81°, N-m-4-*xylyl*-, m.p. 132—132·5°, N-o-, m.p. 75·5—76°, N-m-, m.p. 88·2—88·7°, and N-p-*chlorophenyl*-, m.p. 56·5—57·1°, N-p-*bromophenyl*-, m.p. 78·8—79·3°, N-p-*iodophenyl*-, m.p. 83·6—84·2°, N-m-*nitrophenyl*-, m.p. 126·7—127°, N-p-*dimethylaminophenyl*-, m.p. 108·6—109·3°, N-p-*anisyl*-, m.p. 55·6—56·2°, N-p-*carbethoxyphenyl*-, m.p. 125—125·4°, N-α-, m.p. 107·3—107·7°, and N-β-*naphthyl*-, m.p. 110—110·4°, N-*pentamethylene*-, m.p. 55·5—56·2°, and N-2-*pyridyl*-, m.p. 130·7—131·2°, -N′N′-*dimethylsulphamide*. $NHPh{\cdot}SO_2{\cdot}NMe_2$ and AcCl give the N-*Ac* derivative, m.p. 92·3—92·7°. These products are more stable than $SO_2(NH_2)_2$. They are sol. without decomp. in cold, conc. H_2SO_4. Those containing at least one H attached to N are sol. in dil. alkali. With the exceptions noted, m.p. are corr. R. S. C.

***N*-Chlorocarbamic esters.** P. Chabrier (*Ann. Chim.*, 1942, [xi], **17**, 353—370).—Partly an account of work previously abstracted (A., 1943, II, 82). *NN*-Dichlorocarbamates, $NCl_2{\cdot}CO_2R$, are prepared from $NH_2{\cdot}CO_2R$, NaOCl, and aq. H_2SO_4 or AcOH; thus prepared is *β-chloroethyl* NN-*dichlorocarbamate* (**I**), m.p. 38°. $NCl_2{\cdot}CO_2Et$ (**II**) and styrene in C_6H_6 afford *Et* N-*chloro*-N-β-*chloro*-β-*phenylethylcarbamate*, a liquid (not distillable), reduced by $NaHSO_3$ to *Et* N-β-*chloro*-β-*phenylethylcarbamate*, m.p. 50°, convertible by Na_2CO_3 or $AgNO_3$ in aq. EtOH into the corresponding *β-OH*-ester, m.p. 85°, or by Zn–aq. NH_3 into $Ph{\cdot}[CH_2]_2{\cdot}NH{\cdot}CO_2Et$. Similarly prepared are *Et* N-*chloro*-N-β-*chloro*-β-m-*anisyl*-, and -β-*methylenedioxyphenyl*-α-*methylethylcarbamate*, and *Et* N-β-*chloro*-β-m-*anisyl*- *and* -β-*methylenedioxyphenyl*-α-*methylethylcarbamate*, m.p. 76° and 114°, respectively. $NCl_2{\cdot}CO_2Me$ (**III**) and $(C_2H_4Cl)_2S$ in C_6H_6 give *tetrachlorodiethyl sulphide*, b.p. 115°/15 mm., which decomposes to HCl and

$CH_2Cl{\cdot}CHCl{\cdot}S{\cdot}CH{:}CHCl$. Carbazole and (**III**) in AcOH give *tetrachlorocarbazole*, m.p. 212°; $CH_2Ph{\cdot}CO{\cdot}NH_2$ in H_2O yields *phenylacetchloroamide*, m.p. 120°; 3 : 5-diketo-6-alkyl-1 : 2 : 4-triazine in alkali affords 2 : 4-*dichloro*-3 : 5-*diketo*-6-*benzyl*-, m.p. 119° (explodes at 150°), and -6-*phenylethyl*-1 : 2 : 4-*triazine*, m.p. 130° (explodes at 165°); similarly prepared is 2-*chloro*-3 : 5-*diketo*-4 : 6-*dibenzyl*-1 : 2 : 4-*triazine*, m.p. 153°; 1 : 3-*dichloro*-5 : 5-*diphenylhydantoin*, m.p. 166°, is obtained from diphenylhydantoin; indole-2-carboxylic acid or its Me ester in AcOH yields probably 2 : 3 : (?)5-*trichloro*-2 : 3-*oxido*-2 : 3-*dihydroindole*, m.p. 188° [Zn–AcOH give (?)5-*chloro*-2 : 3-*oxido*-2 : 3-*dihydroindole*, m.p. 192°], or *Me* 2 : 3 : (?)5-*trichloro*-3-*hydroxy*-2 : 3-*dihydroindole*-2-*carboxylate*, m.p. 184°, respectively. (**II**) and aq. glycine give $CH_2(NH{\cdot}CO_2Et)_2$, readily decomposed to CH_2O. $NCl_2{\cdot}CO_2R$ and $NH_2{\cdot}CO_2R$ give $NHCl{\cdot}CO_2R$, which with NaOEt–EtOH–Et_2O afford $NNaCl{\cdot}CO_2R$. *Na Et* N-*chlorocarbamate*, deflagrates at 140°, is prepared. $NNaCl{\cdot}CO_2Me$ and $AsPh_3$ in C_6H_6 give N-*triphenylarsine Me carbamate*, $CO_2Me{\cdot}N{:}AsPh_3$, m.p. 84°, readily hydrolysed to $NH_2{\cdot}CO_2Me$ and $AsPh_3O$. Also prepared (method : *loc. cit.*) are N-*carbethoxy*-N-3-*pyridylcarbamide*, m.p. 200°, N-*carbomethoxy*-, m.p. 100°, and N-*carbethoxy*-N′-*ethoxymethyl*-, m.p. 82°, N-*carbomethoxy*-, m.p. 65°, N-*carbethoxy*-, m.p. 40°, and N-*carbo*-β-*chloroethoxy*-N′-α-*ethylpropyl*-, m.p. 108·5°, and N-*carbomethoxy*-, m.p. 133·5°, and N-*carbethoxy*-N′-*benzyl*-*carbamide*, m.p. 93°. Also prepared are *ethoxymethyl*-, m.p. 132° (*CHPh:* derivative, m.p. 167°), *benzyl*-, m.p. 171° (*semicarbazones* from $COMe_2$, m.p. 151°, PhCHO, m.p. 194°, *p*-$OMe{\cdot}C_6H_4{\cdot}CHO$, m.p. 192°, *p*-$C_6H_4Pr^{\beta}{\cdot}CHO$, m.p. 174°, and $CH_2Ph{\cdot}CO{\cdot}CO_2H$, m.p. 204°), and *phenyl-carbamylsemicarbazide* (**IV**), m.p. 228° (*semicarbazones* from $COMe_2$, m.p. 214°, PhCHO, m.p. 233°, *p*-$OMe{\cdot}C_6H_4{\cdot}CHO$, m.p. 215°, and COPhMe, m.p. 212°). Prolonged action of N_2H_4 on $NHPh{\cdot}CO{\cdot}NH{\cdot}CO_2Me$ liberates NH_2Ph. Derivatives of (**IV**) are converted by Na–Hg into (probably) a *bis*(*phenylcarbamylsemicarbazide*), $(NHPh{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}NH)_2$, m.p. 263°, which does not combine with RCHO. $NNaCl{\cdot}CO_2Me$ and $CO_2Na{\cdot}CR{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2$ in H_2O yield ketotriazoles, $CR{<}\begin{matrix}N{-}NH\\ NH{\cdot}CO\end{matrix}$ A. T. P.

Copper complexes of sulphanilamide and sulphathiazole. W. R. Todd (*Arch. Biochem.*, 1944, **4**, 343—346).—Cryst. complexes of Cu and sulphanilamide or sulphathiazole are prepared by the action of glucose and an alkaline Cu reagent. Both complexes are stable in alkaline solution, but are insol. and unstable in org. solvents and H_2O. Mineral acid decomposes the complexes producing Cu_2O. The sulphanilamide *complex*, $(C_6H_8O_2N_2S)_2Cu_3(OH)_2$, decomp. ~200°, darkens on drying; the sulphathiazole *complex*, $(C_9H_9O_2N_3S_2)Cu$, decomp. ~300°, remains white, and can be obtained in white, yellow or orange crystals, identical microscopically. E. R. S.

Bacterial chemotherapy. IV. Synthesis of N^1:N^4-diacylsulphanilamides. S. Rajagopalan (*Proc. Indian Acad. Sci.*, 1944, **19**, **A**, 343—350).—Sulphanilamide or its N^4-acyl derivative with the appropriate acid chloride in C_5H_5N gives N^1-*acetyl*-, m.p. 166—169° decomp.), N^1-n-*butyryl*-, m.p. 164—168°, N^1-n-*heptoyl*-, m.p. 148—152°, N^1-*palmityl*-, m.p. 123—126°, N^1-*stearyl*-, m.p. 127—130°, N^1-*benzoyl*-, m.p. 180—183°, N^1-*hexahydrobenzoyl*-, m.p. 185—187°, N^1-*cinnamoyl*-, m.p. 228—231°, N^1-α-*naphthoyl*-, m.p. 154—157°, -m-*nitrobenzoyl*-, m.p. 173—178°, and N^1-p-*nitrobenzoyl*-N^4-*hexoyl*-, m.p. 222—230°, and N^1 : N^4-*dihexoyl*-, m.p. 164—172°, -*di*-n-*butyryl*-, m.p. 217—220°, -*di*-n-*heptoyl*-, m.p. 131—134°, -*dibenzoyl*, m.p. 239—240°, -*dihexahydrobenzoyl*-, m.p. 248—250°, -*dicinnamoyl*-, m.p. 216—218°, -*di*-p-*nitrobenzoyl*-, m.p. 251 (decomp.), and *di-furoylsulphanilamide*, m.p. 255° (decomp.), and N^1 : N^4-*di*-p-*nitrobenzoylsulphapyridine*, m.p. 232—234° (decomp.). The mechanism of the action of the sulphonamides is discussed. F. R. S.

***N*-Sulphanilylcarbamides.**—See B., 1944, II, 304.

***N*^{1}-Sulphanilyl*iso*thiocarbamides.** P. C. Guha, P. L. N. Rao, and V. Mahadevan (*Current Sci.*, 1943, **12**, 325—326).—*p*-$NHAc{\cdot}C_6H_4{\cdot}SO_2Cl$ and $NH_2{\cdot}C(SR){:}NH,HCl$ (or HBr), after hydrolysis with 8—10% aq. HCl, yield N^1-*sulphanilyl*-*propyl*-, m.p. 133—134° (*Ac* derivative, m.p. 174°), -*butyl*-, m.p. 116° (*Ac* derivative, m.p. 157°), and -*allyl*-isothiocarbamide, m.p. 170° (*Ac* derivative, m.p. 173—174°). The Et analogue, m.p. 155—156° (Ac derivative, m.p. 180—181°), is prepared similarly (cf. Winnek *et al.*, A., 1942, II, 400), but p-*acetamidobenzenesulphonylbenzyl*isothiocarbamide, m.p. 171—173°, is hydrolysed to *p*-$NH_2{\cdot}C_6H_4{\cdot}SO_3H$ and $CH_2Ph{\cdot}SH$. A. T. P.

Sulphanilylguanidine.—See B., 1944, III, 237.

Guanidine derivatives.—See B., 1944, II, 305.

Preparation of *p*-substituted aromatic ethylene derivatives. R. o (*Chem.-Ztg.*, 1943, **67**, 81).—Heating aromatic ketones or aldehydes with MgMeBr (prep. in Et_2O, subsequently removed) in C_6H_6 gives good yields of olefine. Details are given for (*p*-$NMe_2{\cdot}C_6H_4)_2C{:}CH_2$. R. S. C

Ethylenediamine derivatives having trypanocidal action. A. Funke, and Montezin [with, in part, Viaud and Horclois] (*Ann. Inst. Pasteur*, 1943, **69**, 358—371).—CH_2PhCl (1 mol.; 12 g.) and $(CH_2{\cdot}NH_2)_2,H_2O$ (4 mols.) in EtOH at 120° give $CH_2Ph{\cdot}NH{\cdot}[CH_2]_2{\cdot}NH_2$ (1945 F) (6 g.), b.p. 125—130°/10 mm. (dihydrochloride, m.p. ~255°), and $(CH_2Ph{\cdot}NH{\cdot}CH_2)_2$, b.p. ~190°/10 mm. Similar preps., best at room temp., lead to N-p-*methyl*- (2156 F), b.p. 140°/13 mm. (dihydrochloride, m.p. ~205°), *N*-*p*-ethyl- (2440 RP) [*dihydrochloride*, m.p. 216—218° (decomp.)], N-p-n- (1986 F), b.p. 145—150°/8 mm., and N-p-iso-*propyl*- (**I**) (1921 F) (65—70%), b.p. 145—150°/8 mm. [*dihydrochloride*, m.p. ~235° (decomp.)], N-p-sec.-*butyl*- (2463 RP), b.p. 130—135°/1·3 mm., N-p-*benzyl*- (2160 F), b.p. 200—202°/2·5 mm. (dihydrochloride, m.p. ~230°), N-p-β-*phenylethyl*- (2162 F), b.p. 228—235°/10 mm., N-p-cyclo*pentyl*- (1971 F), b.p. 180—196°/14 mm., N-p-cyclo*hexyl*- (**II**) (1955 F), b.p. 187—190°/7 mm., N-2 : 5- (2152 F), b.p. 155—160°/16 mm. [dihydrochloride, m.p. 255° (decomp.)], and N-2 : 4-*dimethyl*- (2157 F), b.p. 150—154°/13 mm., N-2 : 4 : 6-*trimethyl*- (2163 F), b.p. 160—164°/12 mm., N-2-*methyl*-5-iso*propyl*- (1988 F), b.p. 165°/10 mm., N-4-*methoxy*-2-*methyl*-5-iso*propyl*- (1997 F), b.p. 190—195°/12 mm., N-2-nitro-4-*iso*propyl- (**III**) (2172 F) [*dihydrochloride*, m.p. ~170° (decomp.)], N-2-amino-4-*iso*propyl- (2083 F) [prep. from (**III**) by H_2–Raney Ni in aq. EtOH] [*dihydrochloride*, m.p. 220° (decomp.)], *N*-*p*-nitro- [*dihydrochloride* (2170 F), m.p. ~218°], and thence *N*-*p*-amino- [*dihydrochloride* (2075 F), m.p. 200—235°], N-p-*cyano*- (2097 F), b.p. 160—170°/1·6 mm. (*dihydrochloride*, m.p. ~260°), and N-p-*chloro*- (2115 F), b.p. 135°/2 mm., -*benzylethylenediamine*. Similarly are prepared *N*-*p*-xenylmethyl- (2462 RP) [*dihydrochloride*, m.p. ~295° (block)], N-*tetrahydro*-β-*naphthylmethyl*- (1993 F), b.p. 170—175°/0·8 mm., N-α-*naphthylmethyl*- (1990 F), b.p. 200°/14 mm., N-4-iso*propyl*-1-*naphthylmethyl*- (1999 F), b.p. 187°/6 mm., N-*citronellyl*- (2015 F), b.p. 156—160°/24 mm., and N-β-p-iso*propylphenylethyl*- (2146 F), b.p. 170°/18 mm., -*ethylenediamine*. *p*-$C_6H_4Pr^{\beta}{\cdot}CH_2Cl$ (1 mol.) and $NH_2{\cdot}[CH_2]_2{\cdot}NEt_2$ (2 mols.) give exothermally N-p-iso*propylbenzyl*-N′N′-*diethylethylenediamine* (1964 F), b.p. 155°/8 mm. The appropriate di(chloromethyl) compound leads to 2 : 5-*di*-(β-*aminoethylaminomethyl*)-p-*xylene* (2154 F), b.p. 190—192°/0·7 mm., 4 : 6-*di*-(β-*aminoethylaminomethyl*)-m-*xylene* (2158 F), b.p. 200—205°/1·52 mm., *di*-(x-β-*aminoethylaminomethylphenyl*)*methane* (2159 F), b.p. 250—260°/0·6 mm., and αβ-*di*-(x-β′-*aminoethylaminomethylphenyl*)*ethane* (2161 F), b.p. 255—268°/0·8 mm. CH_2ArCl and the appropriate diamine give δ-p-iso*propylbenzylamino*-α-*diethylamino*-n-*pentane* (1989 F) (prep. at 130°), b.p. 170—172°/8 mm. (hygroscopic dihydrochloride), 1-p-iso*propylbenzylpiperazine* (1966 F), b.p. 165°/13 mm., and N-p-iso*propylbenzylhexamethylenediamine* (1994 F), b.p. 190°/1·2 mm. Heating $OH{\cdot}CH(CH_2Cl)_2$ (1 mol.) and $CH_2Ar{\cdot}NH_2$ (4 mols.) slowly to ~150° gives αγ-*dibenzylamino*- (2079 F), b.p. 217—220°/8 mm., αγ-*di*-p-iso*propylbenzylamino*- (2080 F), and αγ-*di*-p-cyclo*hexylbenzylaminopropan*-β-*ol* (2081 F). As by-products are obtained NN′-*di*-p-n-[*dihydrochloride* (1987 F)] and NN′-*di*-p-iso-*propylbenzyl*- (1943 F), b.p. 230—240°/8 mm. (dihydrochloride), NN′-di-2 : 5-dimethylbenzyl- (2153 F), *NN*′-di-2-nitro-4-*iso*-propylbenzyl- [*dihydrochloride* (2173 F), m.p. 210° (decomp.)], *NN*′-di-*p*-nitrobenzyl- [*dihydrochloride* (2171 F), m.p. ~260° (decomp.)], NN′-*di*-p-*chlorobenzyl*- (2116 F), m.p. 120°, and *NN*′-di(tetrahydro-β-naphthylmethyl)-, b.p. 240—250°/0·8 mm. [*dihydrochloride* (2001 F)], -ethylenediamine and NN′-*di*-p-iso*propylbenzylhexamethylenediamine* (1995 F), b.p. 250—260°/2 mm. Treating (**I**) with, successively, PhCHO, Na_2CO_3–Et_2O–BzCl (later at the b.p.), and 0·1N-HCl gives N-*benzoyl*-N-p-iso*propylbenzylethylenediamine hydrochloride*, m.p. 166°. BzCl and (**I**) in C_6H_6 give the Bz_2 derivative, m.p. 121°. With $CHEt_2{\cdot}CHO$ and then $Na{-}C_5H_{11}{\cdot}OH$, (**I**) gives *N*-*p*-*iso*propylbenzyl-*N*′-β-ethyl-*n*-butylethylenediamine [*dihydrochloride* (1947 F), m.p. ~255° (decomp.)]. Boiling the dihydrochloride of (**II**) with $CN{\cdot}NH_2$ (? in a solvent) gives β-p-cyclo*hexylbenzylaminoethylguanidine dihydrochloride* (1968 F), cryst. For pharmacological data see A., 1944, III, 830. R. S. C.

***p*-Diazonium tertiary amines.**—See B., 1944, II, 304.

Phenol synthesis and catalyst.—See B., 1944, II, 305.

Thymol and *iso*propyl-*m*-cresols obtained from *m*-cresol by condensation reactions. A. E. Tschitchibabin [with C. Barkovsky] (*Ann. Chim.*, 1942, [xi], **17**, 316—334).—*m*-Cresol (**I**) and $Pr^{\beta}OH$–H_3PO_4 (*d* 1·8) at 50—60° or 65—75° for 20 or 14 hr., respectively, then at 18° for 36 hr., give 1 : 4 : 3- (thymol) (**II**), 1 : 6 : 3- (*p*-thymol) (**III**), m.p. 114°, and 1 : 2 : 3-$C_6H_3MePr^{\beta}{\cdot}OH$ (*o*-thymol) (**IV**), m.p. 69° [*NO*-derivative, m.p. 178° (block)]. (**I**) and H_2SO_4 (*d* 1·84) at 120—125° for 2—3 hr., followed by $Pr^{\beta}OH$ at 70—85°, give (**III**) + (**IV**); the use of 100% H_2SO_4 or 35% oleum at ~80° yields (**II**) + (**III**); $C_6H_2MePr^{\beta}{}_2{\cdot}OH$ (**V**) are also formed. Many experiments under varying conditions are recorded. The isomerides obtained depends on the relative amounts of *m*-cresolsulphonic acids formed, the concn. of H_2SO_4, and duration of heating. (**II**) and (**III**) are isolable from (**I**)–$Pr^{\beta}OH$ and H_2SO_4–$Na_2S_2O_7$ at 60—70°. 3 : 1 : 4-$OH{\cdot}C_6H_3Me{\cdot}SO_3H$ (A., 1942, II, 223) and $Pr^{\beta}OH$–100% H_2SO_4 at 65—70° for 3·5 hr. afford 10% of (**IV**), 13% of (**III**), and (**V**); 3 : 1 : 6-$OH{\cdot}C_6H_3Me{\cdot}SO_3H$ gives 25% of (**II**), 12% of (**III**), and (**V**), and the 4 : 6-disulphonic acid yields some (**II**), (**III**), and (**IV**); in all cases, neutral products are also formed. (**I**)–$Pr^{\beta}Cl$–$AlCl_3$–$C_2H_4Cl_2$ at −11° to −13° gives (**II**), (**III**), and a little 1 : 3 : 5-

$C_6H_3MePr^{\beta}\cdot OH$ (*m*-thymol) (**VI**), m.p. 51°; (**VI**) increases in amount as the temp. of reaction rises, and is the main product at room temp. The most stable $C_6H_3MePr^{\beta}\cdot OH$ is (**VI**), which can be obtained from the other isomerides and $AlCl_3$ at 30°. (**III**) [and (**VI**)] is unchanged on heating at 350—400°, but in presence of $ZnCl_2$–fuller's earth at the same temp., conversion into (**VI**) occurs. A. T. P.

Condensation of *tert.*-butyl chloride with *m*-cresol and of *iso*propyl chloride with *m*-4-xylenol. A. Tschitchibabin and C. Barkovsky (*Ann. Chim.*, 1942, [xi], **17**, 349—352).—$Bu^{\gamma}Cl$, *m*-cresol (**I**), and $AlCl_3$ in $C_2H_4Cl_2$ at −13° (7 hr.), then at room temp. (15 hr.), yield (probably) 5-tert.-*butyl*-m-*cresol*, m.p. 50°, b.p. 128°/13 mm.; with H_3PO_4–$Bu^{\gamma}OH$, (**I**) yields 1 : 4 : 3-$C_6H_3MePr^{\beta}\cdot OH$, m.p. 23° (cf. A., 1936, 602), and a small amount of an isomeride, probably 1 : 6 : 3-$C_6H_3MeBu^{\gamma}\cdot OH$. *m*-4-Xylenol and $Pr^{\beta}Cl$–$AlCl_3$–$C_2H_4Cl_2$ at 9—12° give (?)5-iso*propyl*-, m.p. 46—47°, and a *di*iso*propyl*-m-4-*xylenol*, m.p. 99°. A. T. P.

***cyclo*Hexyl sulphite.**—See A., 1944, II, 318.

Nitration of *p*-diphenylyl acetate. S. E. Hazlet, D. A. Stauffer, L. C. Hensley, and H. O. Van Orden (*J. Amer. Chem. Soc.*, 1944, **66**, 1245—1247).—*p*-$C_6H_4Ph\cdot OAc$ (**I**) is more difficult to nitrate than *p*-$C_6H_4Ph\cdot OH$. With conc. HNO_3 in AcOH at 100° (6 hr.) and then room temp. (2 days) it gives some 4 : 3 : 5 : 1-$OH\cdot C_6H_3(NO_2)_2\cdot C_6H_4\cdot NO_2$-*p* (**II**), and other conditions usually give only (**II**). Adding (**I**) to HNO_3 (*d* 1·479) in AcOH at 100° gives (**II**) and a small amount of 4-*nitro*-4′-*acetoxydiphenyl*; m.p. 138—139°. Steric effects are responsible for these results and the difference from bromination. 3-*Nitro*-, m.p. 85—86°, 3 : 5-, m.p. 129—130°, and 3 : 4′-*dinitro*-, m.p. 137—138°, and 3 : 5 : 4′-*trinitro*-, m.p. 148—149°, -4-*acetoxydiphenyl* are obtained from the phenols by boiling Ac_2O–NaOAc. R. S. C.

Action of hydriodic acid on phenolic pinacols and pinacolins. Synthesis of œstrogenic compounds. E. Adler, H. von Euler, and G. Gie (*Arkiv Kemi, Min., Geol.*, 1944, **18**, **A**, No. 1, 21 pp.).—$[OH\cdot C_6H_4\cdot CMe(OH)]_2$ is converted by red P and HI (*d* 1·96) at 135—140° in presence or absence of AcOH into PhOH, meso-$\beta\gamma$-4 : 4′-*dihydroxydiphenylbutane* (**I**), m.p. 231—233° (*diacetate*, m.p. 138—140°; sparingly sol. Na salt), a *compound* (**II**), $C_{16}H_{18(16)}O_2$, m.p. 174—175° (*diacetate*, m.p. 117—118·5°; *dibenzoate*, m.p. 151—151·5°), and r-$\beta\gamma$-4 : 4′-*dihydroxydiphenylbutane* (**III**), m.p. 139—139·5° (also + $CHCl_3$) (*dibenzoate*, m.p. 144—145°). These compounds are also prepared similarly from $\gamma\gamma$-*di*-p-*hydroxyphenylbutan*-β-*one* (**IV**), m.p. 130°, which therefore represents the first step in the change. The next step is not $\gamma\gamma$-*di*-p-*hydroxyphenylbutan*-β-*ol*, m.p. 147—148° (obstinately retains solvent of crystallisation; *dibenzoate*, m.p. 163—164°), obtained by reducing (**IV**) with Na and $C_5H_{11}\cdot OH$ at 140°, since this does not give (**I**), (**II**), or (**III**) with P–HI. Reduction of $(p\text{-}OH\cdot C_6H_4\cdot CMe{:})_2$ (**V**) gives mainly resin from which (**I**) can be isolated in very small amount. The smooth production of (**III**) from (**V**) and H_2–Pd in AcOH establishes the constitution of the former. $[p\text{-}OH\cdot C_6H_4\cdot CEt(OH)]_2$ with red P and HI affords PhOH, δ-p-*hydroxyphenylhexan*-γ-*one*, m.p. 67—68° [*monobenzoate*, m.p. 66—67°; *oxime* (? mixture of forms), m.p. 84—86°, softens at 74°], and a *substance*, $C_{18}H_{20(22)}O_2$, m.p. 226—227° (slight decomp.) (*diacetate*, m.p. 102—104°, softens at 101°). The mechanism of the reactions is discussed (see also A., 1944, III, 810). H. W.

Rearrangement of *iso*dialkylstilbœstrols to dialkylstilbœstrols.—See B., 1944, III, 216.

(A) Mechanism of the cleavage of ethers of the anisole type by Grignard mixtures. (B) Action of Grignard solutions on α-bromoketones. A. Schonberg and R. Moubasher (*J.C.S.*, 1944, 462—463).—(A) PhOMe and related substances undergo fission with Et_2O–Mg halides, resembling that with Grignard mixtures: PhOMe + $MgHal_2$ → $[MgHal\cdot OPhMe]^+Hal^-$ → $PhO\cdot MgHal$ + MeHal. Et_2O–MgI_2 is more effective than Et_2O–$MgBr_2$ at 200—220°. $PhO\cdot CH_2\cdot CH{:}CH_2$ with Et_2O–$MgBr_2$ at 95° (in CO_2) similarly gives PhOH and $CH_2{:}CH\cdot CH_2Br$.

(B) $COPh\cdot CPh_2Br$ with MgI_2 (not $MgBr_2$) in boiling Et_2O, or $MgBr_2$ in warm PhOMe, gives $COPh\cdot CHPh_2$. Analogous reactions with α-Br-ketones and Grignard mixtures is attributed to the $MgHal_2$ present. P. T. C.

Reduction by dissolving metals. I. A. J. Birch (*J.C.S.*, 1944, 431—436).—Methoxyalkyl- (*A*) and alkyl-benzenes with Na in liquid NH_3 in presence of MeOH, EtOH, or *tert.*-$C_5H_{11}\cdot OH$ as proton source undergo a 1 : 4-addition of 2 H [the products from (*A*) being converted into Δ^2-*cyclo*hexenones with dil. acid and determined with 2 : 4 : 1-$(NO_2)_2C_6H_3\cdot NH\cdot NH_2$ or $NH_2\cdot CO\cdot NH\cdot NH_2$]. (*A*) also give ~10% of the phenol by demethylation. α-$C_{10}H_7\cdot ONa$ with *tert.*-$C_5H_{11}\cdot OH$ thus gives 5 : 8-dihydro-α-naphthol, m.p. 74°; Na alone gives little reduction. β-$C_{10}H_7\cdot ONa$ gives 2-keto-1 : 2 : 3 : 4-tetrahydronaphthalene, b.p. 140°/13—14 mm.; in absence of alcohol some of an ar-*dihydro*-2-*methoxynaphthalene*, b.p. 145—150°/14 mm., is obtained after methylation (Me_2SO_4) of the alkali-sol. product. α-$C_{10}H_7\cdot CO_2Na$ is readily reduced in absence of alcohol to 1 : 4-m.p. 75°, and, after treatment with 20% NaOH at 100° (bath), 3 : 4-dihydro-α-naphthoic acid, m.p. 112°.

Reducing *m*-$C_6H_4Me\cdot OMe$ (**I**) in presence of MeOH yields 1-methyl-Δ^1-*cyclo*hexene and 3-*methyl*-2 : 5-*dihydroanisole*, b.p. 170—171°, characterised as 3-methyl-Δ^2-*cyclo*hexenone [*semicarbazido-semicarbazone*, m.p. 210° (decomp.); 2 : 4-*dinitrophenylhydrazone*, m.p. 173°]; in absence of MeOH ~50% of (**I**) is converted into *m*-$C_6H_4Me\cdot ONa$. 6-Methoxy-1 : 2 : 3 : 4-tetrahydronaphthalene gives 2-keto-$\Delta^{1:9}$-octahydronaphthalene (MgMeI–CuBr gives *cis*-2-keto-9-methyldecahydronaphthalene), but no ketonic product was obtained from the 6-methoxy-5-methyl derivative. Amongst other compounds similarly prepared, the following are new: 2 : 6-, m.p. 210—211°, 4 : 6-, m.p. 175°, and (?) 3 : 4-*dimethyl*-Δ^2-cyclo*hexenone*-*semicarbazone*, m.p. 193°; (?) 3 : 6-*dimethyl*-Δ^2-cyclo*hexenone*-*semicarbazidosemicarbazone*, m.p. 214° (decomp.) and -2 : 4-*dinitrophenylhydrazone*, m.p. 134°; 6-*methyl*-Δ^2-cyclo*hexenone*-2 : 4-*dinitrophenylhydrazone*, m.p. 122—126°; 5-*keto*-$\Delta^{4:9}$-*tetrahydrohydrindene*-*semicarbazone*, m.p. 228—230°, and -2 : 4-*dinitrophenylhydrazone*, m.p. 197—198°. With EtOH, reduction converts *m*-xylene into 2 : 5-dihydro-*m*-xylene (ozonolysis yielding CH_2Ac_2) [*nitrosochloride*, m.p. 123° (decomp.); *nitrolpiperidine*, m.p. 137°], *p*-xylene into (? 2 : 5-)dihydro-*p*-xylene (nitrosochloride, m.p. 98°; nitropiperidine, m.p. 133°), tetrahydronaphthalene into 1 : 2 : 3 : 4 : 5 : 8-hexahydronaphthalene (*nitrosochloride*, m.p. 91°), and *p*-cymene into a product (25—30%) containing γ-terpinene (nitrosochloride, m.p. 110°; nitrolpiperidine, m.p. 144°). A rule correlating reduction products with the position of substituents is stated. P. T. C.

Oxidation [of dienes].—See A., 1944, II, 317.

Photochemical properties of 1 : 4-dimethoxy-9 : 10-diphenylanthracene.—See A., 1944, I, 290.

Colchicine and related compounds. Synthesis of 2 : 3 : 4 : 5-, 2 : 3 : 4 : 6-, and 2 : 3 : 4 : 7-tetramethoxy-9-methylphenanthrene.—See A., 1944, II, 314.

***o*-*p*′-Nitrobenzamidophenol: a correction.** L. C. Raiford and N. N. Crounse (*J. Amer. Chem. Soc.*, 1944, **66**, 1240—1241).—*o*-$NH_2\cdot C_6H_4\cdot OH$ and *p*-$NO_2\cdot C_6H_4\cdot COCl$ (**I**) in dioxan–$NPhMe_2$ (cooling) give o-p′-*nitrobenzamidophenol* (**II**) (77%), m.p. 202—203°, converted by (**I**) in $CHCl_3$–C_5H_5N exothermally into o-p′-*nitrobenzamidophenyl* p-*nitrobenzoate* (**III**), m.p. 219°. The compound, m.p. 219—220°, supposed by Tingle *et al.* (A., 1907, i, 209) to be (**II**) was (**III**), but the mother-liquors obtained by their method contain some (**II**), m.p. 203—204°. *o*-$NH_2\cdot C_6H_4\cdot OMe$ and (**I**) in C_5H_5N–dioxan give o-p′-*nitrobenzamidoanisole*, m.p. 145·5—146°, also obtained from (**II**) by NaOMe–MeI–MeOH. R. S. C.

Structure and properties of azo-β-naphthol dyes. V. N. Ufimtzev (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, **39**, 351—353).—Absorption curves are compared for the azo- and hydrazone forms of 4 : 1-$NPh{:}N\cdot C_{10}H_6\cdot OH$ and 1-*p*-sulphobenzeneazo-β-naphthol (Na and Na_2 salt, $+2H_2O$), and 1-*m*-sulphobenzeneazo-2-naphthol-3-carboxyanilide (Na, $+H_2O$, and Na_2 salt, $+1{\cdot}5H_2O$). The Na and Na_2 salts are formed in neutral aq. solution and EtOH–NaOEt, respectively; in dil. aq. or EtOH alkali the Na and Na_2 salts are in equilibrium. The difference in structure of *o*- and *p*-azonaphthol dyes is apparent from the shift of the absorption max. which occurs on salt formation and ionisation. With *p*-azo-dyes, the shift is towards the long-wave side; with *o*-azo-dyes it is to the opposite side in accordance with a chelate structure. A. T. P.

Bacterial chemotherapy. V. Synthesis of phenolic azo-dyes derived from sulphonamides. S. Rajagopalan (*Proc. Indian Acad. Sci.*, 1944, **19**, **A**, 351—356).—The following are prepared from *p*-$NHR\cdot SO_2\cdot C_6H_4\cdot N_2Cl$ and the appropriate phenol: *mono*- and *di*-p-*sulphamylbenzeneazoresorcinol*; p-*sulphamylbenzeneazo-thymol*, -*phloroglucinol*, -α-*naphthol*, and -3-*phenanthrol*; 2 : 4-*dihydroxy*-4′-*guanidinosulphonyl*-, -4′-2″-*pyridyl*-, -4′-2″-*thiazolyl*-, and -4′-2″-*thiazolinyl*-*sulphamylazobenzene*; 8-*hydroxy*-5-p-2′-*thiazolylsulphamylbenzeneazoquinoline*. F. R. S.

Azo-compounds from *o*-nitrothiophenol and its methyl ether. C. Simons and L. G. Ratner (*J.C.S.*, 1944, 421—422).—*o*-$NO_2\cdot C_6H_4\cdot Sn$ (**I**) with *n*-$C_5H_{11}\cdot ONa$ in $C_5H_{11}\cdot OH$ at 130° gives Na_2 *azobenzene*-2 : 2′-*disulphinate* (**II**), which gives a pink free acid [dimorphous (probably) Me_2 esters, m.p. 135° and 195°, with CH_2N_2]. Acid or alkaline reduction of (**II**) or the Me esters failed to give *o*-$NH_2\cdot C_6H_4\cdot SO_2H$. *o*-$NO_2\cdot C_6H_4\cdot SMe$ (**III**) with $C_5H_{11}\cdot ONa$ similarly gives no sulphone but 2 : 2′-*di*(*methylthiol*)-*azobenzene*, m.p. 153—155°, and -*azoxybenzene*, m.p. 78—80° (separated by chromatographic analysis), with some *o*-$NH_2\cdot C_6H_4\cdot SMe$. Enolisation of the NO_2 group of (**I**) may occur; this cannot occur with (**III**). P. T. C.

Sulphones.—See B., 1944, III, 238.

Vinyl alcohols. XI. β-Phenyl-β-mesitylvinyl alcohol. R. C. Fuson, N. Rabjohn, and D. J. Byers. **XII. Oxidation of αα-diarylethylenes.** R. C. Fuson, M. D. Armstrong, W. E. Wallace, and J. W. Kneisley (*J. Amer. Chem. Soc.*, 1944, **66**, 1272—1274, 1274—1276).—XI. *β-Phenyl-β-mesitylvinyl alcohol* (**I**) resembles $CMes_2{:}CH\cdot OH$ (Mes = mesityl here and below). *α-Phenyl-β-mesitylethylene glycol* (cf. Weinstock, *Thesis*, 1936), m.p. 144—146°, is obtained from $COPh\cdot COMes$ by H_2–Cu chromite in EtOH at 150°/2200 lb. or from $COPh\cdot COMes$ or $COMes\cdot CHPh\cdot OH$ by H_2–PtO_2;

with H_2SO_4–AcOH it gives $CH_2Mes{\cdot}COPh$ but with boiling conc. HCl–AcOH yields (I), m.p. 114—115°. (I) is unchanged at 175°, in conc. aq. NH_3 at 100° gives *di-β-phenyl-β-mesitylvinyl ether*, m.p. 172—174°, is not affected by O_2 in Et_2O or light petroleum (23 hr.), P–I, or hot KOH–MeOH, but slowly decomposes in air; with MgMeI it yields 0·87 CH_4. With HCl–EtOH or –MeOH it gives the *Et*, b.p. 169—170°/2 mm., or *Me ether*, m.p. 44—45°, b.p. 144—145°/0·1 mm. (oxidised by SeO_2 in boiling dioxan to COPh·COMes), respectively. In Ac_2O–C_5H_5N at room temp. (I) gives the *acetate* (II), m.p. 91—92°, with BzCl–C_5H_5N–$CHCl_3$ at the b.p. and then room temp. gives the *benzoate*, m.p. 117—117·5°, and with H_2–Raney Ni in EtOH at 150°/1700 lb. yields *β-phenyl-β-mesitylethyl alcohol*, b.p. 170—173°/4 mm. (*p-nitrobenzoate*, m.p. 124—125°). (I) is oxidised by O_3 in $CHCl_3$ to $CHPhMes{\cdot}CO_2H$ [also obtained similarly from (II)] and COPh·CHMes·OH, by $KMnO_4$–$COMe_2$ to a saturated *compound*, $C_{34}H_{34}O_2$, m.p. 152—153° (decomp.), by NaOCl to COPh·COMes, by H_2–Ni–NaOH–MeOH–H_2O to COPhMes, and by CrO_3 to an oil and small amounts of a *compound*, $(C_{12}H_{12}O)_x$, m.p. 204—205° (decomp.), and COPh·COMes. (I) has absorption max. at 2·76 and 2·84 μ. due to the OH.

XII. O_3 converts some sterically hindered $CAr_2{:}CH_2$ into $CAr_2{:}CH{\cdot}OH$. Thus, $CPhMes{:}CH_2$ gives (I), m.p. 114—115° (corr.), and small amounts of COPh·COMes and $CHPhMes{\cdot}CO_2H$, and *α-iso*durylstilbene gives *β-phenyl-β-isodurylvinyl alcohol* (III) (20%), m.p. 121·5—122°, and *phenyl*isodurylacetic *acid* (IV), m.p. 198—198·5°. With Ac_2O–C_5H_5N, (III) gives the *acetate*, m.p. 93—93·5°, with MgMeI gives 1 CH_4, and with H_2–Raney Ni in EtOH at 50°/1000 lb. gives *β-phenyl-β-isodurylethyl alcohol*, m.p. 72—73°. (IV) is also obtained from *iso*durene (V) by OH·CHPh·CO_2H and $SnCl_4$ or, by way of its *Et* ester, m.p. 57·5—58°, b.p. 188—189°/6 mm., by $CHPhBr{\cdot}CO_2H$ etc. O_3 converts *p*-$C_6H_4Me{\cdot}CMes{:}CH_2$ into *p-tolylmesitylacetic acid*, m.p. 211—212°, but no vinyl alcohol is obtained. $CH_2Ph{\cdot}COCl$–$AlCl_3$ converts (V) into iso*duryl CH₂Ph ketone*, m.p. 60·5—61° [and (?) *di*(*phenylacetyl*)iso*durene*, m.p. 137—137·5°], oxidised by SeO_2 and a little H_2O in boiling dioxan to syn- and anti-*Ph* iso*duryl diketone*, m.p. (VI) 65—66° (*oxime*, m.p. 87—87·5°) and 63—63·5° (*oxime*, m.p. 129·5—130°) or vice versa. *iso*Durylglyoxal, C_6H_6, and $AlCl_3$ at room temp. give 2 : 3 : 4 : 6-*tetramethylbenzoin*, m.p. 92—93° (*dibenzoate*, m.p. 133—135°, of the enediol), oxidised by I–NaOMe in boiling MeOH to (VI). H_2–Raney Ni in EtOH at 150—175°/2000 lb. reduces (VI) to *α-phenyl-β-isodurylethylene glycol*, m.p. 131·5—132°, whence boiling, conc. HCl–AcOH yields (III).

R. S. C.

Acyloxyaralkyl nitriles.—See B., 1944, II, 305.

Antibacterial action of derivatives and analogues of *p*-aminobenzoic acid. O. H. Johnson, D. E. Green, and R. Pauli (*J. Biol. Chem.*, 1944, **153**, 37—47).—See A., 1944, III, 830. The following are stated to be new (analyses given) but no details of prep. are recorded: 4-*amino*-2-*acetamidobenzoic acid*, m.p. 205°; p-*acetamidomethylbenzoic acid*, m.p. 191°; 2-p-*aminobenzamidothiazole*, m.p. 257—258°; p-*aminobenzoyl*-l-*glutamic acid*; 5-*nitrothiophen*-2-*carboxylamide*, m.p. 191°; 5-*aminothiophen*-2-*carboxylamide hydrochloride*; 5-*acetamido*-2-*thienyl Me ketone*, m.p. 279°; 2-*aminothiazole*-5-*carboxylic acid*, m.p. 191°. M.p. are corr.

E. C. W.

Preparation and catalytic reduction of γ-nitro-β-butyl *p*-nitrobenzoate.—See A., 1944, II, 317.

Oxidation of aromatic amino-acids, tyrosine, tryptophan, and phenylalanine. B. B. Drake and C. V. Smythe (*Arch. Biochem.*, 1944, **4**, 255—263).—Phenylalanine is not oxidised by $KMnO_4$ or cerox (Ce^{III} NH_4 sulphate). Tryptophan shows no end-point with 4 equivs. of either oxidant. Tyrosine shows an end-point with 3 equivs. of cerox; the impure oxidation product was isolated, some of its properties are described, and an oxidation mechanism is suggested.

E. R. S.

Mono-iodotyrosine. C. R. Harington and (Mrs.) R. V. Pitt Rivers (*Biochem. J.*, 1944, **38**, 320—321).—Diazotisation [$Ba(NO_2)_2$ in dil. H_2SO_4] of 3-amino-*l*-tyrosine and treatment with KI and Cu-bronze gives 3-*iodo*-l-*tyrosine*, m.p. 204—206° (decomp.), $[\alpha]_D^{20}$ −4·4° in N-HCl. 3-*Nitro*-dl-*tyrosine*, m.p. 214—215° (decomp.) (prep. from *dl*-tyrosine and dil. HNO_3 at <25°), is reduced to the NH_2-compound, m.p. 288° (decomp.), and converted into the *I*-derivative (+H_2O), m.p. 200—201° (decomp.), which appears to be identical with the compound obtained by Ludwig *et al.* (A., 1939, II, 369). That isolated by Herriott (A., 1942, III, 172) is not identical with either of the compounds.

F. R. S.

***In-vitro* formation of thyroxine from di-iodotyrosine.**—See A., 1944, III, 728.

Acetolysis of esters. S. G. Cohen (*J. Amer. Chem. Soc.*, 1944, **66**, 1396—1397).—After boiling in AcOH–Ac_2O (35 : 2 by vol.) for 20 hr. 17% of $Bu^{\gamma}OBz$ was recovered, 87% of the remainder was isolated as BzOH but only 8·5% of $Bu^{\gamma}OAc$ was formed. After keeping for 2 days with a little *p*-$C_6H_4Me{\cdot}SO_3H$ (I) in Ac_2O–AcOH at room temp. only 25% of $Bu^{\gamma}OBz$ is recovered, and of the remainder 82% is obtained as $Bu^{\gamma}OAc$, 61% as BzOH, and 6·5% as $CMe_2{:}CH_2$; acetolysis is rapid at the b.p. (76% in 2·5 hr.) but no $Bu^{\gamma}OAc$ is obtained. With (I) in boiling Ac_2O–AcOH for 24 hr. 69·7% of $Pr^{\beta}OBz$ is unchanged and of the remainder 57% appears as BzOH and 58% as $Pr^{\beta}OAc$; EtOBz and MeOBz are substantially (88%) unchanged under these conditions and no ROAc or BzOH is obtained. $Pr^{\alpha}CO_2Et$ is unchanged by KOAc in boiling Ac_2O–AcOH, but only 55% of $CCl_3{\cdot}CO_2Bu$ is recovered after similar treatment, 65% of the remainder being obtained as BuOAc. $CCl_3{\cdot}CO_2Bu$ is unaffected by (I) in AcOH at 115°. Reaction mechanisms are discussed.

R. S. C.

Derivatives of dialkoxyphthalides. R. H. F. Manske and A. E. Ledingham (*Canad. J. Res.*, 1944, **22**, **B**, 115—124).—2 : 3 : 1-$(OMe)_2C_6H_3{\cdot}CO_2H$, HCl, and 40% CH_2O yield 3 : 4-*dimethoxy*-6-*chloromethylphthalide* (CO=2) (I), m.p. 106°, *di*-(4 : 5-*dimethoxy*-3-*carboxy*-2-*hydroxymethylbenzyl*) *ether dilactone*, m.p. 213°, and a little meconine. Reduction (Zn–HCl–EtOH) of (I) affords 3 : 4-*dimethoxy*-6-*methylphthalide*, m.p. 127°, also prepared from 2 : 3 : 5 : 1-$(OMe)_2C_6H_2Me{\cdot}CO_2H$, CH_2O, and HCl. 3 : 2 : 1-$OMe{\cdot}C_6H_3(OEt){\cdot}CO_2H$ with CH_2O–HCl yields 4-*methoxy*-3-*ethoxy*-6-*chloromethylphthalide* (II), m.p. 130°, hydrolysed (H_2O) to the 6-*OH*·CH_2 derivative, m.p. 120°, and converted by MeOH–NaCN into 4-*methoxy*-3-*ethoxy*-6-*cyanomethylphthalide*, b.p. 145°/2 mm., m.p. 132°, which is hydrolysed (NaOH) to 4-*methoxy*-3-*ethoxy*-6-*carboxymethylphthalide*, m.p. 151°. Reduction of (II) with Zn–HCl–EtOH gives 4-*methoxy*-3-*ethoxy*-6-*methylphthalide* (III), m.p. 119°. 2 : 5 : 3 : 1-$OH{\cdot}C_6H_2Me(OMe){\cdot}CHO$ (IV), m.p. 77° (improved prep.; lit., an oil) (*oxime*, m.p. 165°), is methylated (Me_2SO_4–NaOH) to 2 : 3-*dimethoxy*-5-*methylbenzaldehyde*, m.p. 40° (*oxime*, m.p. 99°), which with $CH_2(CO_2H)_2$, C_5H_5N, and piperidine gives 2 : 3-*dimethoxy*-5-*methylcinnamic acid*, m.p. 188°, reduced (Na–Hg) to *β*-2 : 3-*dimethoxy*-5-*methylphenylpropionic acid*, m.p. 63°. 3-*Methoxy*-2-*ethoxy*-5-*methylcinnamic acid*, m.p. 168°, prepared by ethylation of (IV) followed by $CH_2(CO_2H)_2$ etc., is reduced (Na–Hg) to *β*-3-*methoxy*-2-*ethoxy*-5-*methylphenylpropionic acid*, m.p. 100°. Oxidation ($KMnO_4$) of 3 : 5 : 2 : 1-$OMe{\cdot}C_6H_2Me(OEt){\cdot}CHO$ gives 3-*methoxy*-2-*ethoxy*-5-*methylbenzoic acid*, m.p. 89°, which with CH_2O–HCl yields (III). Creosol acetate with $AlCl_3$ in $PhNO_2$ at 80° gives 3-*hydroxy*-4-*methoxy*-6-*methylacetophenone*, m.p. 129°, with a little of the 3 : 4-(*OH*)$_2$-derivative, m.p. 169°, both of which with Me_2SO_4–NaOH give 3 : 4-*dimethoxy*-6-*methylacetophenone*, m.p. 76°. This yields *oximino*-3 : 4-*dimethoxy*-6-*methylacetophenone*, m.p. 122°, hydrolysed (NaOH) to 3 : 4 : 6 : 1-$(OMe)_2C_6H_2Me{\cdot}CO_2H$. The following are also described; 3-*methoxy*-2-*ethoxycinnamic acid*, m.p. 152° [from the aldehyde and $CH_2(CO_2H)_2$], reduced (Na–Hg) to *β*-3-*methoxy*-2-*ethoxyphenylpropionic acid*, m.p. 64°; 4-*methoxy*-3-*ethoxy*-2-*methylcinnamic acid*, m.p. 186°, reduced to *β*-4-*methoxy*-3-*ethoxy*-2-*methylphenylpropionic acid*, m.p. 121°; 2-*methoxy*-3-*ethoxycinnamic acid*, m.p. 184°, reduced to *β*-2-*methoxy*-3-*ethoxyphenylpropionic acid*, m.p. 66°. 2-*Methoxy*-3-*ethoxybenzoic acid*, m.p. 64°, is prepared by oxidation of the aldehyde. M.p. are corr.

J. D. R.

Iodinated acyltaurines.—See B., 1944, III, 237.

Sulphamide-amidines. I. *p*-Sulphamylbenzamidine and related compounds. R. Delaby and J. V. Harispe (*Bull. Soc. chim.*, 1943, [v], **10**, 580—584).—*p*-$CN{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$ and HCl in abs. EtOH at 0° give the hydrochloride, m.p. ~174° (freshly prepared; loses HCl when kept and melts at 182—183°), of the *imino Et ether*, m.p. 157°, converted by NH_3 in abs. EtOH into p-*sulphamylbenzamidine*, m.p. 251° (*hydrochloride*, m.p. 242°).

A. T. P.

Theory of biogenesis of lichen depsides and depsidones. T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1944, **20**, **A**, 1—14).—Lichen depsides and depsidones are considered to arise from a common source, 2 : 3 : 5 : 1-$CHO{\cdot}C_6H_2(OH)_2{\cdot}CH_2{\cdot}OH$, which originates from aldol condensation between a hexose and a biose with elimination of H_2O. Oxidation and reduction lead to various modifications of this unit and increase in the length of the side-chain arises from condensation with simple sugars and reduction. Depsides are formed by the combination of two of these units. β-Orcinol derivatives are obtained by nuclear methylation by CH_2O and this reaction in general takes place prior to depside formation, though the other possibility is not altogether excluded as far as the left half of the mol. is concerned. Depsidones come last in the evolution; they are based on depsides and require oxidation or dehydrogenation involving $C_{(5)}$ which is *para* to the activating OH. Nuclear oxidation also occurs without leading to depsidone formation; either $C_{(3)}$ or $C_{(5)}$ is involved and *meta*-depsides result. Oxidation involving the left half is also possible and is represented by diploschistesic acid. The occurrence of orcinol and psoromic acid is attributed to decarboxylation occurring in the plant.

H. W.

Preparation of homophthalyl and 4-aminohomophthalyl cyclic hydrazides. W. F. Whitmore and R. C. Cooney (*J. Amer. Chem. Soc.*, 1944, **66**, 1237—1240).—*o*-$CO_2H{\cdot}C_6H_4{\cdot}CH_2{\cdot}CO_2H$ (I), readily obtained in 58% yield from indene by $K_2Cr_2O_7$–H_2SO_4–H_2O at the b.p., with AcCl or, better, Ac_2O gives the anhydride (II), which with $N_2H_4{,}H_2O$ in boiling EtOH yields cyclic *homophthalhydrazide* (III) (80%), m.p. 298—300°. (III) could not be obtained from the Me_2 ester or imide of (I) and the diacid chloride of (I) could not be prepared. (III) behaves as a monoenol towards aq. NaOH (phenolphthalein); it gives no Ac derivative but in boiling AcOH gives

N-*aminohomophthalimide*, m.p. 147—148° (N'-*Ac* derivative, m.p. 239—240°), which is also obtained from (II) by N_2H_4,H_2O in boiling AcOH. 2 : 4 : 1-$CO_2H{\cdot}C_6H_3(NO_2){\cdot}CH_2{\cdot}CO_2H$ [obtained from (I) by fuming HNO_3 or, better, KNO_3–H_2SO_4] in boiling AcCl gives the *anhydride* (70%), m.p. 154—155°, which with N_2H_4,H_2O in AcOH at 100° gives cyclic 4-nitrohomophthalhydrazide (70%), amorphous, m.p. 248—250° (decomp.), reduced by H_2–Raney Ni in aq. NaOH to cyclic 4-*aminohomophthalhydrazide*, m.p. 210—212° (decomp.; rapid heating) or decomp. ~200—320° (slow heating) (N^4-*Ac* derivative, m.p. >320°). With H_2O_2–NaOH the cyclic hydrazides are much less luminescent than is phthalhydrazide. R. S. C.

Nitrones. III. Condensation of 2 : 4 : 6-trinitrotoluene with arylnitroso-compounds. I. Tanasescu and I. Nanu (*Ber.*, 1942, **75**, [*B*], 1287—1292; cf. A., 1939, II, 323).—Contrary to Radulescu *et al.* (A., 1939, II, 537), nitrones and not additive NH_2OH compounds are formed from 1 : 2 : 4 : 6-$C_6H_2Me(NO_2)_3$ (I) and *o*-, *m*-, or *p*-$C_6H_4Me{\cdot}NO$ or *p*-$NO{\cdot}C_6H_4{\cdot}NMe_2$ (II). (I) and *o*-$C_6H_4Me{\cdot}NO$ in boiling EtOH containing Na_2CO_3 or piperidine or in C_5H_5N containing I at 40—50° afford 2 : 4 : 6-*trinitrophenyl*-N-*o-tolylnitrone*, m.p. 147—148° (explosion), the constitution of which follows from its behaviour when heated, its partial hydrolysis by HCl to 2 : 4 : 6 : 1-$(NO_2)_3C_6H_2{\cdot}CHO$ (III), and its isomerisation by AcCl in hot $COMe_2$ to 2 : 4 : 6-*trinitrobenz-o-toluidide*, m.p. 259° (decomp.) (*Ac* derivative, m.p. 200°), identical with the product obtained from 2 : 4 : 6 : 1-$(NO_2)_3C_6H_2{\cdot}COCl$ and *o*-toluidine in boiling C_6H_6. 2 : 4 : 6-*Trinitrophenyl*-N-m-*tolylnitrone*, m.p. 157° (explosion), obtained similarly, is isomerised to 2 : 4 : 6-*trinitrobenz-m-toluidide*, m.p. 209·5° (*Ac* derivative, m.p. 185°). Similarly 2 : 4 : 6-*trinitrophenyl*-N-p-*tolylnitrone*, m.p. 151° (explosion), is isomerised to 2 : 4 : 6-*trinitrobenz-p-toluidide*, m.p. 217° (*Ac* derivative, m.p. 210°). With $NHPh{\cdot}NH_2$ in acid solution all these nitrones afford 2 : 4 : 6 : 1-$(NO_2)_3C_6H_2{\cdot}CH{:}N{\cdot}NHPh$ in small yield. Hydrolysis is accompanied by a marked phenolic odour. (I) and (II) gives the somewhat unstable 2 : 4 : 6-trinitrophenyl-*N*-*p*-dimethylaminophenylnitrone, characterised by its tendency towards explosion and hydrolysis to (III) and *p*-$NH_2{\cdot}C_6H_4{\cdot}NMe_2$. H. W.

Synthesis of aromatic amino-aldehydes and amino-ketones. W. Hao-Tsing (*J. Amer. Chem. Soc.*, 1944, **66**, 1421—1422).—When NH_2Ph is gently heated with HCN–HCl–Et_2O, a brown oil is pptd., which, when further heated at 250—300° and then boiled in aq. KOH, gives *p*-$NH_2{\cdot}C_6H_4{\cdot}CHO$. NH_2Ph with MeCN–HCl–Et_2O similarly gives *p*-$NH_2{\cdot}C_6H_4{\cdot}COMe$. Reagents and conditions must be anhyd. The oily intermediates are probably $NH{:}CR{\cdot}NHPh$, rearranged by heat to *p*-$NH_2{\cdot}C_6H_4{\cdot}CR{:}NH$, which is hydrolysed by the KOH. The reaction may be general. R. S. C.

Structure of *o*-hydroxybenzaldazines. H. von Euler, E. Adler, and J. Ettlinger (*Arkiv Kemi, Min., Geol.*, 1944, **17**, **A**, No. 16, 15 pp.).—1 : 4 : 2 : 6-$OH{\cdot}C_6H_2Me(CHO)_2$ (I) and $COEt{\cdot}NH{\cdot}NH_2$ or $(CO{\cdot}NH{\cdot}NH_2)_2$ in dil. EtOH give respectively *hydroxyuvitinaldehydedi*(*propionylhydrazone*) (II), m.p. 239—241° (also +2AcOH), and amorphous polyhydroxyuvitinaldehydedi(oxalylhydrazone) (III), no definite m.p. (II) is converted readily by boiling dil. mineral acid into *hydroxyuvitinaldazine* (IV), m.p. 278—280°, best obtained by the gradual addition of $N_2H_4,2HCl$ in 50% EtOH to (I) in the same solvent. Under similar conditions (III) affords polyhydroxyuvitinaldazine (V), decomp. >360°, also obtained from (I) and N_2H_4,H_2O in EtOH or, preferably, in presence of AcOH; it has pronounced indicator properties. (IV) is sparingly sol. in dil. NaOH, freely in KOH; it cannot be methylated by CH_2N_2 or KOH–Me_2SO_4 and does not give an Ac derivative. The stability of (IV) and (V) towards dil. mineral acids suggests the possibility of a quinonoid structure, which, however, is less probable for (V). This hypothesis is strengthened by the less intense colour of *methoxyuvitinaldazine* (VI), m.p. 234—235°, and the amorphous polymethoxyuvitinaldazine (VII) obtained from methoxyavitinaldehyde and N_2H_4 in acid and neutral solution, respectively. The hydrochloride of (V) is very stable towards heat (117°/12 mm.); this property is shared to some extent by the hydrochloride of *o*-methoxybenzaldazine but not by those of (IV), (VI), (VII), salicylaldazine, and benzaldazine. Examination of the equilibrium $(CHR{:}N{\cdot})_2 + 2H_2O \rightleftharpoons 2RCHO + N_2H_4$ in presence of acid shows no difference in stability between hydroxy- and methoxy-aldazines. Since only the aldazine structure is possible for the latter compounds there appears no reason to assume a peculiar (quinoid) constitution for the former substances and the greater resistance of the azomethine group (in comparison with PhCHO) must be ascribed to steric hindrance. The most probable structure for *o*-hydroxyaldazines is the "normal" benzenoid form with co-ordinatively united bridge H. The individuality of (IV) is in harmony with the occurrence of mesomerism. *Methoxyuvitinaldehydedi*(*propionylhydrazone*) has m.p. 295°. H. W.

2 : 3 : 5 : 8-Tetramethoxy-6 : 7-dimethyl-1-naphthaldehyde. R. Adams and Z. W. Wicks (*J. Amer. Chem. Soc.*, 1944, **66**, 1315—1316).—Attempts to prepare OH-naphthaldehydes having the properties of gossypol failed. Pure *o*-xyloquinone and $[CH_2{:}C(OMe)]_2$ at 140° give 6 : 7-dimethoxy-2 : 3-dimethyl-1 : 4-naphthaquinone (I) (77—82·5%), m.p. 248—249° (lit. 241—242°), which by hydrogenation (H_2–Raney Ni; MeOH; 50°/1500 lb.) and thereafter immediate methylation (Me_2SO_4–KOH–H_2O–$Na_2S_2O_4$) yields 1 : 4 : 6 : 7-*tetramethoxy*-2 : 3-*dimethylnaphthalene* (73%), m.p. 151—152°. With $HCO{\cdot}NPhMe$ and $POCl_3$ at the b.p. this gives 2 : 3 : 5 : 8-*tetramethoxy*-6 : 7-*dimethyl*-1-*naphthaldehyde* (67%), m.p. 135—136°, which yields normally a *phenylhydrazone*, m.p. 156—157°, and *oxime*, m.p. 155—156° (with boiling Ac_2O yields 2 : 3 : 5 : 8-*tetramethoxy*-6 : 7-*dimethyl*-1-*naphthonitrile*, m.p. 122·5—123°). Reductive acetylation of (I) gives 1 : 4-*diacetoxy*-6 : 7-*dimethoxy*-2 : 3-*dimethylnaphthalene* (91%), m.p. 180·5—181°. No cryst. phenols could be obtained from the OMe-products. M.p. are corr. R. S. C.

Cinnamylideneacetone tetrabromide. P. Duquénois and Z. Sezer (*Rev. Fac. Sci. Istanbul*, 1943, **8**, **A**, 158—159).—$CHPh{:}CH{\cdot}CH{:}CH{\cdot}COMe$ and Br in Et_2O give a red oil from which *cinnamylideneacetone tetrabromide*, m.p. 173·5° (slight decomp.) (cf. Diehl *et al.*, A., 1885, 1221), is isolated by repeated crystallisation from EtOH. H. W.

Synthesis of model substances for the ligninsulphonic acids. Synthesis of α-phenylacetone-α-sulphonic acid and propioveratrone-α-sulphonic acid. A. von Wacek, K. Kratzl, and A. von Bezard (*Ber.*, 1942, **75**, [*B*], 1348—1357).—$CHPhAcBr$, from CH_2PhAc and Br in anhyd. Et_2O, is converted by KCNS in EtOH into α-thiocyano-α-phenylacetone (I), m.p. 51—52°, and by KSAc and KSBz in EtOH into α-*acetylthiol*- (II), b.p. 157—158°/12 mm., m.p. 31°, and α-*benzoylthiol*-, m.p. 58°, -α-*phenylacetone*, respectively. (II) is smoothly hydrolysed by alkali (but not by acid) to α-*thiol*-α-*phenylacetone* (III), m.p. 108—110° (*Hg* derivative, m.p. 124—126°). Chlorination of an aq. suspension of (I) gives, in proportion varying with the experimental conditions, $CHPhAcCl$, unchanged material, and an α-*thiocyano*-α-*chlorophenylacetone*, m.p. 56·5°. Similar treatment of (II) affords $CHPhAcCl$ and somewhat impure (?) αα-*dichloro*-α-*phenylacetone*, m.p. 120—125° (oxidation gives BzOH). Oxidation of (III) with NaOCl in C_6H_6–Et_2O–H_2O gives the *disulphide*, m.p. 108°, and a residue converted into an unidentified *benzylthiuronium* salt, m.p. 164°. Similar treatment of (II) appears to give no disulphide; mixtures of benzylthiuronium salts which cannot be separated are obtained. A well-stirred mixture of $CHPhAcBr$ and boiling aq. Na_2SO_3 gives *Na* α-*phenylacetone*-α-*sulphonate*, m.p. 204—206°, isolated through the *benzylthiuronium* salt, m.p. 140—141°. Similarly bromopropioveratrone affords *Na propioveratrone*-α-*sulphonate* (corresponding *benzylthiuronium* salt, m.p. 153°). H. W.

New reagent for primary and secondary amines. A. J. Birch (*J.C.S.*, 1944, 314—315).—*cyclo*Hexene nitrosochloride warmed with C_5H_5N gives 1-(2'-*oximinocyclohexyl*)*pyridinium chloride* (+H_2O), m.p. 125°, which when heated in 10% Na_2CO_3 with the hydrochloride of the base gives 2-*oximinocyclohexyl* derivatives (m.p. in parentheses) of the following: $NHMe_2$ (120°), NH_2Pr^{α} (72°), NH_2Bu^{α} (81°), NH_2Bu^{β} (73°), NH_2Bu^{γ} (91°), $NHEt_2$ (63°), morpholine (118°), and *n*-$C_5H_{15}{\cdot}NH_2$ (66°). The derivative from piperidine has new m.p. 116° (lit. 119°). *cyclo*Hexylamine gives 2-*oximinodicyclohexylamine*, m.p. 145°. E. W. W.

Synthesis of possible degradation products of metathebainone. II. H. L. Holmes and L. W. Trevoy (*Canad. J. Res.*, 1944, **22**, **B**, 109—114; cf. A., 1944, II, 281).—$(CH_2{\cdot}CO)_2O$ and veratrole yield (method: Fieser *et al.*, A., 1937, II, 20) β-3 : 4-*dimethoxy*- (I) and some β-4-*hydroxy*-3-*methoxy-benzoylpropionic acid* (II), m.p. 131—131·5°, reduced (Clemmensen) to γ-4-*hydroxy*-3-*methoxyphenylbutyric acid*, m.p. 114—116°. (II) with KOH–Et_2SO_4 gives β-3-methoxy-4-ethoxybenzoylpropionic acid, m.p. 139—140° (lit. 136—137°), the orientation of which is proved by oxidation ($KMnO_4$) of the Et ester to 3 : 4 : 1-$OMe{\cdot}C_6H_3(OEt){\cdot}CO_2H$, also prepared from vanillin. Prep. of (I) is modified to give 83%. M.p. are corr. J. D. R.

Stereochemistry of cyclanes. XII. Polybenzyl*cyclo*hexanones; isolation of four *o*-dibenzyl*cyclo*hexanones of which three are almost certainly 2 : 6-derivatives. R. Cornubert, P. Anziani, M. Andre, M. de Demo, and G. Morelle (*Bull. Soc. chim.*, 1943, [v], **10**, 561—565; cf. A., 1939, II, 164).—The 2 : 6-dibenzyl*cyclo*hexanone (I), new m.p. 105° (*oxime*, m.p. 123°; *semicarbazone*, m.p. 164—165°) (cf. A., 1939, II, 324), prepared by benzylation of 2-benzyl*cyclo*hexanone, could not be obtained by hydrogenating dibenzylidene*cyclo*hexanone; the latter method affords isomerides, m.p. 122° and 55°, of (I) (cf. A., 1934, 279), convertible by CH_2PhCl–$NaNH_2$–Et_2O into 2 : 2 : 6-tribenzyl-, m.p. 61—62°, and 2 : 2 : 6 : 6-tetrabenzyl-*cyclo*hexanone (II), m.p. 174°. (II) is also obtained by dibenzylating (I) or the 2 : 2-isomeride, m.p. 69—70° (cf. A., 1932, 161). (I) is not isomerised by HCl. With Na–EtOH, (I) yields probably an impure *sec.* alcohol, but with H_2–PtO_2–Et_2O it gives probably a 2 : 6-dihexahydrobenzyl*cyclo*hexanol (*phenylurethane*, m.p. 132—134°). P

Synthesis of compounds related to santonin. (Miss) K. D. Paranjape, N. L. Phalnikar, B. V. Bhide, and K. S. Nargund (*Proc. Indian Acad. Sci.*, 1944, **19**, **A**, 381—384).—α-(2-Hydroxy-4-formyl-3-keto*cyclo*hexyl)propiolactone, $COMe_2$, and EtOH–NaOEt give α-1-*hydroxy*-4-*keto*-$\Delta^{5:8}$-*hexahydro*-2-*naphthylpropiolactone*, m.p. 91°; COMeEt similarly affords the corresponding 8-*Me* derivative, m.p. 111. α-(2-Hydroxy-4-formyl-3-keto-4-methyl*cyclo*hexyl)propiolactone

condenses similarly with $COMe_2$ to *α-1-hydroxy-7-keto-10-methyl-*$\Delta^{5:8}$*-hexahydro-2-naphthylpropiolactone*, m.p. 141° (semicarbazone, m.p. 201°). F. R. S.

3 : 4-Benzfluorenones. I. Effect of groups on their formation and their fission with alkali. F. G. Baddar and M. Gindy (*J.C.S.*, 1944, 450—452).—Factors governing the point of cleavage of 3 : 4-benzfluorenones and mode of cyclisation of 1-phenylnaphthalene-2'-carboxylic acids are of polar, and not steric, origin. 4 : 2-$C_{10}H_6I{\cdot}OMe$ (**I**) and *o*-$C_6H_4I{\cdot}CO_2Me$ with Cu-bronze at 200—210° give *3-methoxy-1-phenylnaphthalene-2'-carboxylic acid*, m.p. 191—192°, cyclised (P_2O_5–C_6H_6) to *1-methoxy-3 : 4-benzfluorenone*, m.p. 148—150°, and 2-methoxy*meso*benzanthrone (little). 3 : 1 : 2-$C_6H_3I(CO_2Et)_2$ with 1-$C_{10}H_7I$ and Cu-bronze at 210° (bath) gives 1-phenylnaphthalene-2' : 3'-dicarboxylic acid, m.p. 178—179° (slow), 185°—193° (rapid heating) [*Me*$_2$ ester, m.p. 133—134°; *anhydride* (**II**), m.p. 179—180°]. Cyclisation of (**II**) (CS_2–$AlCl_3$) yields 3 : 4-*benzfluorenone-8-carboxylic acid* (**III**), m.p. 276—276·5° (little), and *meso*benzanthrone-8-carboxylic acid, m.p. 262—263° (lit. 254—255°) (Me ester, m.p. 173·5—174·5°). *1-Phenylnaphthalene-2 : 4'-dicarboxylic acid* (**IV**), m.p. 265—266° (from *p*-$C_6H_4I{\cdot}CO_2Me$ and 1 : 2-$C_{10}H_6Br{\cdot}CO_2Me$), gives on ring-closure (chloride with $AlCl_3$–CS_2) only 3 : 4-*benzfluorenone-7-carboxylic acid* (**V**), m.p. 323—324°. (III) with KOH at 225—230° gives *1-phenylnaphthalene-2 : 3'-dicarboxylic acid*, m.p. 255—256°, whilst (**V**) gives a mixture of (**IV**) and (probably) 1-phenylnaphthalene-2' : 4'-dicarboxylic acid. (**I**) is obtained (diazo-method) in poor yield from 4 : 2-$NH_2{\cdot}C_{10}H_6{\cdot}OMe$ (*Ac* derivative, m.p. 179°); 2-hydroxy-1 : 4-naphthaquinone [which may arise from 1 : 4-$C_{10}H_6(OH)_2$] is isolable from the many by-products. *Et* 3-p-*toluenesulphonamidophthalate* has m.p. 147—148°. P. T. C.

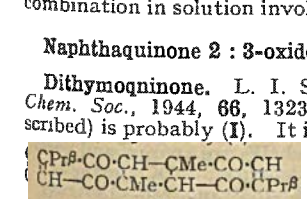
2-Methyl-2-phytyl-2 : 3-dihydro-1 : 4-naphthaquinone.—See B., 1944, III, 218.

Hydrolysis of quinoneoximes. W. T. Sumerford and D. N. Dalton (*J. Amer. Chem. Soc.*, 1944, **66**, 1330—1331).—Hydrolysis of quinone mono-oximes by Cu_2O (1 mol.) in boiling HCl–$COMe_2$–H_2O–methylcellosolve or in HCl–$COMe_2$–H_2O at room temp. gives good yields (55—92% in 9 out of 11 examples) of the parent quinone. The methods of Karrer *et al.* (A., 1939, II, 335) and Tseng *et al.* (A., 1934, 1005; 1944, II, 166) are less satisfactory. R. S. C.

Molecular compounds of the quinhydrone type in solution. L. Michaelis and S. Granick (*J. Amer. Chem. Soc.*, 1944, **66**, 1023—1030).—The absorption of light (λ 300—550 mμ.) by solutions containing mixtures of a quinone (*Q*) with a benzenoid substance (*B*) that combine to form a compound of the quinhydrone type is due almost entirely to the compound, and has been used to detect and obtain a relative measure of the extent of such combination with various pairs of components. It is assumed that the concn. *m* of the compound is always small compared with that of the components, so that the association const. $k = m/[Q][B]$ can be taken to refer to the initial concns. of *Q* and *B*. The measured optical absorption $[(I_0 - I)/I_0]$, after correction (often negligible) for the components, is divided by the known val. of $[Q][B]$ to obtain ε_{st}, which is related to the mol. extinction coeff. $\varepsilon_{mol.}$ for the compound by $\varepsilon_{st} = k\varepsilon_{mol.}$; the vals. of ε_{st} are then $\propto m$, although the abs. val. of *m* is not known. The following pairs of substances were studied in EtOH and, sometimes, in C_6H_6, light petroleum, or 0·05N-HCl: (*a*) *p*-O:C_6H_4:O (**I**)–quinol, (**I**)–resorcinol, *b*-O:C_6Cl_4:O–C_6Me_6, duroquinone–duroquinol; (*b*) (**I**)–PhOH, (**I**)–*p*-$OH{\cdot}C_6H_4{\cdot}OMe$; (*c*) (**I**)–*s*-$C_6H_3(OH)_3$; (*d*) (**I**)–PhOR, (**I**)–*p*-$C_6H_4(OR)_2$ (R = Me, Et). Combination occurs in all the mixtures, and is $\propto$ both [*Q*] and [*B*]; hence the compound formed is in every case *QB*. Since the substances in groups (*a*), (*b*), and (*c*) form solid compounds *QB*, QB_2, and Q_2B respectively, whilst those in (*d*) form no solid compounds, it appears that the structure of the compounds formed in solution differs from that of the solids. H linkings are not necessary, and the affinity of (**I**) for a phenol is approx. the same as for its ethers. It is suggested that combination in solution involves a planar superposition of the rings. F. L. U.

Naphthaquinone 2 : 3-oxides.—See B., 1944, II, 305.

Dithymoquinone. L. I. Smith and R. W. H. Tess (*J. Amer. Chem. Soc.*, 1944, **66**, 1323—1325).—Dithymoquinone (prep. described) is probably (**I**). It is unchanged by H_2SO_4 (little) in Ac_2O, by AcCl or PCl_3 at room temp., H_2SO_4–MeOH, or $FeCl_3$–EtOH at the b.p. It is resinified by HBr–AcOH and converted by $Na_2S_2O_4$ slowly into thymoquinol. It has no characteristic absorption. R. S. C.



(I.)

IV.—STEROLS AND STEROID SAPOGENINS.

Steroids and specificity of the Pettenkofer reaction. I. Qualitative studies. G. W. Kerr and W. M. Hoehn (*Arch. Biochem.*, 1944, 5—158).—The Schmidt modification (A., 1942, III, 755) of Pettenkofer's reaction was applied to 43 steroids; 12 give a positive result. All steroids with OH at $C_{(7)}$, or a group easily converted into OH, give a positive result as well as Δ^3-, Δ^5-, and Δ^8-monocholenic acids and their esters. αβ-Unsaturated ketones gave a negative result. Dehydro-*trans*-androsterone gave a positive result. E. R. S.

Preparation and properties of ergosteryl iodide. A. Jendrassik (*Biochem. Z.*, 1941—1942, **311**, 402—407).—Ergosterol with I powder in a little $CHCl_3$ at room temp. gives a stable *iodide*, $C_{28}H_{44}OI_2$ ($+H_2O$), m.p. 92° (absorption max. at 370 and 298 mμ.), which has no antirachitic power (daily dose 2 μg.) even after irradiation, and is converted by Na_2S–$CHCl_3$–0·1N-HCl (little) into an I-free compound, m.p. 127° [not pptd. by digitonin; absorption max. at 275 mμ.; no antirachitic power (daily dose 2 μg.) even after irradiation]. W. McC.

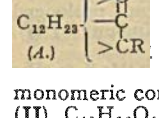
Bile acid derivatives.—See B., 1944, III, 216.

V.—TERPENES AND TRITERPENOID SAPOGENINS.

Halogen derivatives of 1 : 8-cineole. R. Delaby and A. Billuart (*Bull. Soc. chim.*, 1943, [v], **10**, 567—573).—Cineole (**I**) is chlorinated by Cl_2–CCl_4–aq. $CaCO_3$ in sunlight or artificial light (cf. Gandini, A., 1933, 830; 1937, II, 295). Raman spectra of resulting fractions, b.p. (*a*) 118—121°, (*b*) 121—123°, (*c*) 123—125°, (*d*) 125—127°, and (*e*) 127—129°, all at 50 mm., are examined; (*a*) and (*b*) and some of (*c*) probably contain *cis*- and *trans*-2-chlorocineole, and (*d*) and (*e*) the 3-isomeride, but no definite conclusions are reached. Dehalogenation is difficult, but prolonged boiling (90 hr.) with AcOH and AgOAc or KOAc gives some OAc-derivative, b.p. 118—123°/50 mm., hydrolysed by boiling NaOH–MeOH to *cineolic alcohol*, b.p. 108—111°/9 mm. (*allophanate*, m.p. 169°; two *phenylurethanes*, m.p. 140° and 188°, corresponding probably to the *cis*- and *trans*-alcohols). (**I**) and Br–CCl_4–aq. $CaCO_3$ yield some cis- or/and trans-*2-bromocineole*, b.p. 93—95°/4 mm. Oxidation of *l*-pinene or *d*-α-pinene by BzO_2H–$CHCl_3$ gives the respective oxides. Similarly prepared is *αβ-oxidoheptan-γ-ol*, b.p. 86—89°/10 mm., which is hydrolysed by boiling H_2O (+HCl) to *n*-butylglycerol, m.p. 53·5°. Similarly, vinyl*iso*butylcarbinol (*allophanate*, m.p. 147·5°) affords the *oxide*, b.p. 93—97°/20 mm., hydrolysed to iso*butylglycerol*, b.p. 173—174°/16 mm. A. T. P.

Rearrangement of santenonequinone. R. N. Chakravarti (*Current Sci.*, 1944, **13**, 158).—*dl*-Santenonequinone with conc. H_2SO_4 gives 2 : 3-*dimethyl*cyclo*hexan*-1-*one*-4-*carboxylic acid* (**I**), m.p. 132° (*semicarbazone*, m.p. 191°), which is oxidised (HNO_3) to *α-methylbutane-αβδ-tricarboxylic acid*, m.p. 181—182°, also obtained by condensing $Cl{\cdot}[CH_2]_2{\cdot}CO_2Et$ with $CO_2Et{\cdot}CHMe{\cdot}CH(CN){\cdot}CO_2Et$ followed by hydrolysis. Et αβ-dimethylacrylate with $CN{\cdot}CH_2{\cdot}CO_2Et$ and NaOEt affords a Na salt, which with $Cl{\cdot}[CH_2]_2{\cdot}COEt$ yields *Et γ-cyano-αβ-dimethylpentane-αγε-tricarboxylate*, b.p. 200—204°/6 mm. This on hydrolysis and subsequent esterification gives *Et αβ-dimethylpentane-αγε-tricarboxylate*, b.p. 178°/7 mm., which is cyclised (Na) to *Et* 2 : 3-*dimethyl*cyclo*hexan*-1-*one*-4 : 6-*dicarboxylate*, b.p. 170°/8 mm., hydrolysed to (**I**). F. R. S.

Sesquiterpenes. LXIV. Addition of acetylenedicarboxylic ester, azodicarboxylic ester, and maleic anhydride to caryophyllene. P. A. Plattner and L. Werner [with, in part, N. Clauson-Kaas] (*Helv. Chim. Acta*, 1944, **27**, 1010—1016).—Adducts of the type *A* (R = ·N(CO_2Et)·NH·CO_2Et, ·C(CO_2Me):CH·CO_2Me, or ·CH<(CO–O / CH_2–CO)) are



(A.)

described. Caryophyllene *B* (**I**) and $(:C{\cdot}CO_2Me)_2$ at 180° according to experimental conditions give varying amounts of polymeric compounds, possibly owing to the non-homogeneity of (**I**). A mixture of stereoisomerides is probably present in the monomeric condensation product, which gives the dicarboxylic *acid* (**II**), $C_{19}H_{26}O_4$, m.p. 122—123°, [α] +77·2° in $CHCl_3$, in only 25% yield. (**II**) affords a non-cryst. *Me*$_2$ ester, b.p. 180—190°/1 mm., $[\alpha]_D$ +79·3° in $CHCl_3$, which gives a yellow colour with $C(NO_2)_4$. (**II**) is hydrogenated to a non-cryst. H_2-acid, the *Me*$_2$ ester, b.p. ~180°/1 mm., α_D −11°, of which is converted by Mg, MeI, and NH_2Ph into the dianilide, m.p. 228° (vac.), $[\alpha]_D$ +39° in $COMe_2$, identical with the *trans*-tetrahydrodicarboxyanilide obtained from (**I**) and $(:CH{\cdot}CO)_2O$. The adducts from (**I**) and $(:C{\cdot}CO_2Me)_2$ or $(:CH{\cdot}CO)_2O$ therefore have the same C skeleton and must be produced by a similar reaction scheme. (**I**) and $(:N{\cdot}CO_2Et)_2$ react rapidly at room temp. but only ~15% of the product could be isolated as the cryst. *adduct*, $C_{21}H_{34}O_4N_2$, m.p. 139°, $[\alpha]_D$ +39° in $CHCl_3$; this evolves 2 CO_2 when hydrolysed by acid but does not yield cryst. products. The behaviour of $(:N{\cdot}CO_2Et)_2$ indicates the presence of C:C·C in (**I**). Unknown catalytic influences appear to affect the reaction between (**I**) and $(:CH{\cdot}CO)_2O$; the yield of additive product is increased by prolongation of the change and by use of an increased proportion of anhydride, but the quantities of polymeride are also thereby increased. Unchanged (**I**) resembles the original material in *d* and *n* but $[\alpha]_D$ is appreciably lower. Feebly dextrorotatory fractions may be obtained from it by distillation. M.p. are corr. H. W.

Triterpenes. LXXXVIII. Friedelin and cerin. L. Ruzicka, O. Jeger, and P. Ringnes (*Helv. Chim. Acta*, 1944, **27**, 972—988; cf. Drake, A., 1936, 1386).—The presence of the group ·CH_2·CH_2·CO·CH·CH< in friedelin (**I**) and cerin (**II**) which is now established shows that the structure of the terminal ring in these compounds differs from that of the oleanolic series. The isolation of (**I**), m.p. 248—250° (open capillary), 264—265° (vac.), $[\alpha]_D$ −27·8°, and of (**II**), m.p. 250—254° (open capillary), $[\alpha]_D$ −41·2°, from cork is described. *enol*Friedelin benzoate (**III**) has m.p. 246—249° (open capillary), 265—266° (high vac.), $[\alpha]_D$ +64·1°. (**I**) is reduced by N_2H_4,H_2O–NaOEt in EtOH at 200—220° to friedelan, m.p. 243—244°, $[\alpha]_D$ +41·8°, saturated towards $C(NO_2)_4$ and identical with the compound obtained by Clemmensen's method. Under different conditions, oxidation of (**I**) by CrO_3 in AcOH gives varied proportions of friedelonic acid (**IV**) (Me ester, m.p. 153—154·5°, $[\alpha]_D$ +11·8°) and *friedelindicarboxylic acid* (**V**), $C_{30}H_{50}O_4$, m.p. 288° (decomp.), $[\alpha]_D$ +21·4° [*Me*$_2$ ester, m.p. 174—176°, $[\alpha]_D$ +9·8°; *anhydride* (**VI**), m.p. 264—265° (decomp.), $[\alpha]_D$ +74·6°]. (**II**) is oxidised by CrO_3 (=6 O) in AcOH–CCl_4 at room temp. to (**V**) and enol*friedelandione*, $C_{30}H_{48}O_2$, m.p. 265—267°, $[\alpha]_D$ +18·5° (*acetate*, m.p. 283—285°, $[\alpha]_D$ +3°; *benzoate*, m.p. 301—303°, $[\alpha]_D$ +25·7°; *quinoxaline* derivative, m.p. 244—246°), which gives a dark brown colour with $FeCl_3$ and a feebly positive test with $C(NO_2)_4$. (**III**) is oxidised by CrO_3 in AcOH at 100° to (**IV**) and *enol*friedelandione benzoate, m.p. 302—304° (decomp.), $[\alpha]_D$ +24·1°. Thermal decomp. of (**VI**) leads to an amorphous *norfriedelanone* (**VII**) and a fraction, m.p. 231—232°, $[\alpha]_D$ −83·7°, also obtained by subliming (**VI**) at 210°/high vac., showing that CO of (**I**) lies in a terminal ring of the skeleton. SeO_2 in boiling AcOH oxidises (**VII**) to *norfriedelenone*, $C_{29}H_{46}O$, m.p. 260—261°, $[\alpha]_D$ −108°, reduced (Clemmensen) to (**VII**), whereas in dioxan at 200° the oxidation product is *norfriedelenedione* (**VIII**), $C_{29}H_{44}O_2$, m.p. 269—270°, $[\alpha]_D$ +241° (*quinoxaline* derivative, m.p. 240—240·5°), which is saturated towards $C(NO_2)_4$, does not give a colour with $FeCl_3$, cannot be acetylated, and is greatly decomposed by KOH–MeOH. (**III**) is oxidised by SeO_2 in dioxan at 170° to (**VIII**), also obtained by the similar oxidation of *enol*friedelandione benzoate. $Pb(OAc)_4$ or H_2O at 80° oxidises (**VIII**) to a *compound*, $C_{29}H_{44}O_3$, m.p. 236·5—237°, $[\alpha]_D$ −40·9°, which does not give a colour reaction with $C(NO_2)_4$ or $FeCl_3$ and is unaffected by 5% KOH–EtOH at 100°. (**VIII**) is transformed by Br in AcOH into *nordibromofriedelenone*, m.p. 197° (decomp.), $[\alpha]_D$ +63·6°, transformed by boiling KOH–MeOH to enol*norfriedelenedione*, m.p. 260—261°, $[\alpha]_D$ +179·5° [*acetate*, m.p. ~256° (decomp.), $[\alpha]_D$ +208°]. M.p. are corr. $[\alpha]_D$ are in $CHCl_3$. H. W.

Saponins and sapogenins. XXV. Norechino- and *iso*norechinocystenedione. J. F. Carson, D. B. Cosulich, and C. R. Noller. **XXVI. Conversion of echinocystic acid into oleanolic acid.** D. Frazier and C. R. Noller. **XXVII. Structure of triterpenoids.** C. R. Noller (*J. Amer. Chem. Soc.*, 1944, **66**, 1265—1267, 1267—1268, 1269—1271; cf. A., 1944, II, 343).—XXV. *iso*Norechinocystenedione (**I**) is unchanged by hot Ac_2O–C_5H_5N and, except for a little tar-formation, by MeI–Ag_2O, but with boiling Ac_2O–KOAc or HCl–MeOH or –EtOH gives norechinocystenedione (**II**), m.p. 203—205°, $[\alpha]_D^{29}$ −94·2°, $[\alpha]_{5460}^{28}$ −113° in dioxan [dioxime, m.p. 246—249° (decomp.; bath preheated at 225°), $[\alpha]_D^{23}$ −127° to −128°, $[\alpha]_{5460}$ −136° in dioxan]. With BuSH–HCl (but not either alone) in hot EtOH, (**I**) gives a conjugated, isomeric *dione* (**III**), m.p. 236—242°, $[\alpha]_D^{25}$ +45·3°, $[\alpha]_{5460}^{26}$ +56·1° in $CHCl_3$ [*oxime*, m.p. 269—271° (decomp.; bath preheated at 200°), $[\alpha]_D^{25}$ −23·4° in dioxan], having absorption max. at 252 mμ. (log ε 4·10). Purification of (**II**) gives a product having a single absorption max. at 294 mμ. (log ε 1·98) (cf. A., 1939, II, 517); the impurity is not (**III**), since prolonged treatment of (**II**) with alkali yields only a small amount of (**I**). The change, (**I**) ⇄ (**II**), is thus reversible.

XXVI. Me echinocystate acetate, in which the OH β to the CO_2H is free, with $MeSO_2Cl$–C_5H_5N gives *Me echinocystate acetate methanesulphonate* (**IV**), decomp. ~165°, which with NaI in $COMe_2$ at 100° gives *Me anhydroechinocystate acetate* (**V**), m.p. 192—193°, $[\alpha]_D$ +19·5°, $[\alpha]_{5460}$ +22·2° in $CHCl_3$, hydrolysed by hot, conc. HCl–MeOH to *Me anhydroechinocystate* (**VI**), m.p. 177°, resolidifies, remelts at 192—193°, or, after drying at 110°, m.p. 192—193°, $[\alpha]_D^{23}$ +18·3°, also obtained directly from (**IV**) by MeOH at 140°. Hydrogenation (PtO_2; AcOH) of (**VI**) or (**V**) gives Me oleanolate, m.p. 199—200°, $[\alpha]_D^{15}$ +73·2°, $[\alpha]_{5460}^{25}$ +86·7° in $CHCl_3$, and the acetate thereof, m.p. 219—220°, $[\alpha]_D^{24}$ +69·7°, $[\alpha]_{460}^{24}$ +84·7° in $CHCl_3$, respectively. Thus echinocystic acid (**VII**) differs from oleanolic acid only in containing an OH β to the CO_2H.

XXVII. Current formulæ for the triterpenoids of the β-amyrin series are inadequate for (**II**), (**VII**), and various absorption spectra. Absorption max. at 258, 248, and 241 mμ. (log ε 4·31, 4·47, and 4·42, respectively) are recorded for the Me keto-ester, $C_{31}H_{46}O_3$, derived from (**VII**). R. S. C.

VI.—HETEROCYCLIC.

Crossed Cannizzaro reactions—benzaldehyde and furfuraldehyde. S. E. Hazlet and R. B. Callison (*J. Amer. Chem. Soc.*, 1944, **66**, 1248—1250).—Shaking 1 mol. each of PhCHO and furfuraldehyde with aq. NaOH gives a ~5 : 3 mixture of CH_2Ph·OH and furfuryl alcohol and a mixture (~3 : 5) of BzOH and 2-furoic acid. For analysis see C., 1945, Part 1. R. S. C.

Antibacterial substance from *Aspergillus clavatus*. F. Bergel, A. L. Morrison, A. R. Moss, and H. Rinderknecht (*J.C.S.*, 1944, 415—421).—An antibacterial substance, clavatin (**I**), m.p. 109·5—110·5°, has been isolated from *A. clavatus* metabolism solution, and is identical with claviformin and most probably with patulin. Additional evidence is presented for its structure which confirms the formulæ advanced by Raistrick *et al.* (cf. A., 1944, III, 219). The results of oxidative and other degradations suggest the existence of predominant tautomeric forms such as anhydro-4-hydroxy-5-hydroxymethyl- and -5 : 6-dihydro-1 : 2-pyran-6-carboxylic acid. (**I**) is acylated and etherified under unusually mild conditions, forming a monoacetate, *monobenzoate*, m.p. 143·5—144·5°, and *Me$_3$ ether*, m.p. 69—71°; (**I**) forms an *oxime*, m.p. 152—153° (decomp.) (*monoacetate*, m.p. 82—84°). Hydrogenation (≡3—4 H_2) (H_2–Pd-C) of (**I**) in EtOH–H_2O gives a lactone (?) and other products. With HBr the crude hydrogenation product yields a small amount of a *lactone monobromide*, $C_7H_{11}O_3Br$, b.p. 175—180°/15 mm. (*piperidino hydriodide*, $C_{12}H_{22}O_2NI$, m.p. 170—171°), hydrogenated to β-(*a'-bromo-n-propyl*)*butyrolactone*, which affords a phenylhydrazide identical with that from β-*n*-propylbutyrolactone. Ozonolysis of (**I**) gives HCO_2H and glyoxal and traces of $H_2C_2O_4$. HCl (dry) with (**I**) in EtOH at −10° affords an oil, $C_{11}H_{17}O_5Cl$, b.p. 114—116°/0·15 mm. [2 : 4-*dinitrophenylhydrazones* (from EtOH), m.p. 168—170° (decomp.), and (from MeOH), m.p. 164—166° (decomp.) (not identical)], hydrolysed with dil. acid to 3-*chloromethyleneletrahydro-γ-pyrone-2-carboxylic acid*, m.p. 129—130° (2 : 4-*dinitrophenylhydrazone*, m.p. 189—190°). This acid with HI yields ε-iodo-γ-ketohexoic acid and on hydrogenation (H_2–Pd–C) gives 3-*methyltetrahydro-γ-pyrone-2-carboxylic acid* (S-*benzylthiuronium* salt, m.p. 149—150°; p-*phenylphenacyl* ester, m.p. 125—127°; 2 : 4-*dinitrophenylhydrazone*, m.p. 197—199°). The latter acid with HI forms *αε-di-iodo-γ-keto-β-methylhexoic acid*, m.p. 103—105°, hydrogenated to γ-keto-β-methyl-*n*-hexoic acid (S-*benzylthiuronium* salt, m.p. 144·5—145·5°). F. R. S.

Triacetone alcohol and its dehydration products.—See A., 1944, II, 360.

4-Hydroxy-3-methylcoumarin oxime, m.p. 95°.—See A., 1944, III, 717.

Optically active tocols and degradation products of phytol and phytadiene. P. Karrer, A. Kugler, and H. Simon (*Helv. Chim. Acta*, 1944, **27**, 1006—1009).—Slight dextrorotation of εη-dimethyltocol acetate in EtOH and of the εθ-compound in substance is observed but the activity of the ηθ-derivative remains uncertain; the substances are derived from natural phytol. Oxidation ($Na_2Cr_2O_7$–50% H_2SO_4) of Me δθμ-trimethyltridecyl ketone (obtained by ozonolysis of natural *d*-phytol) affords *d*-δθμ-trimethyltridecoic acid (**I**), b.p. 138—144° (bath)/high vac. (p-*bromophenacyl* ester, m.p. 53°; p-*xenylamide*, m.p. 99—100°). Phytadiene is ozonised to (**I**), CH_2O, and small amounts of MeCHO; it therefore consists mainly of Buβ·$[CH_2]_2$·CHMe·$[CH_2]_3$·CHMe·$[CH_2]_3$·CH:CMe·CH:CH_2, with a small proportion of Buβ·$[CH_2]_2$·CHMe·$[CH_2]_3$·CHMe·CH_2·CH:CH·CMe:CHMe. H. W.

Reaction between quinones and metal enolates. XIX. Structure of diduroquinone. L. I. Smith, R. W. H. Tess, and G. E. Ullyot (*J. Amer. Chem. Soc.*, 1944, **66**, 1320—1323; cf. A., 1944, II, 103).—Diduroquinone (**I**), m.p. 207·5—208°, obtained from duroquinone by a little KOH in 95% EtOH at room temp. (cf. Rugheimer *et al.*, A., 1896, i, 68), is probably 7-*hydroxy*-2 : 3 : 5 : 6 : 8 : 4a : 9a-*heptamethyl*-4a : 9a-*dihydroxanthen*-1 : 4-*quinone*. With MgMeI it gives 0·81 CH_4 and 2·05 mols. are added, but this is unreliable since its *Et ether* (prep. by EtBr–KOH in boiling EtOH), m.p. 130—131°, adds 1·84 MgMeI and gives 0·52 CH_4. With hot Ac_2O, (**I**) gives an acetate (**II**), +*x*EtOH, m.p. (dried at 100°) 132—133°. $FeCl_3$ in boiling EtOH oxidises (**I**) to 6-*hydroxy*-5-3' : 4' : 6'-*trimethyl*-2'-p-*benzquinon*-1'-*ylmethyl*-2 : 3-*dimethyl*-5 : 6-*dihydro*-p-*benzoquinone* (**III**), m.p. ~132—138°, reduced by $Na_2S_2O_4$ to 6-*hydroxy*-p-3' : 6'-*dihydroxy*-2' : 4' : 5'-*trimethylbenzyl*-2 : 3-*dimethyl*-5 : 6-*dihydro*-p-*benzoquinone* (**IV**), m.p. ~144—149°, whence H_2SO_4–MeOH at room temp. regenerates (**I**). M.p. of (**III**) and (**IV**) are approx. and variable owing either to decomp. or steric isomerism. $SOCl_2$ at the b.p. converts (**I**) into substances, m.p. 153—155° and 136—138°. (**I**) gives no oxime or dinitrophenylhydrazone, is resinified by boiling KOH–EtOH or conc. H_2SO_4 at 60—65°, is unaffected by HCl–AcOH or HBr–AcOH, and in HI–AcOH gives duroquinol, which is also obtained by H_2–Cu chromite in EtOH, Zn–AcOH, Zn–HCl, or (?) Na–Hg–EtOH (not by $Na_2S_2O_4$) and from (**III**) by Zn–AcOH. (**I**) has an absorption max. at ~290 mμ. (ε ~3000). R. S. C.

4 : 4-Dimethyl-5-ethoxymethyl-*m*-dioxan.—See B., 1944, II, 306.

Synthesis of cantharidin and deoxycantharidin. (Miss) K. Paranjape, N. L. Phalnikar, B. V. Bhide, and K. S. Nargund (*Proc. Indian Acad. Sci.*, 1944, **19**, A, 385—388).—(CMeAc·CO_2Et). (from

CNaMeAc·CO_2Et and I in C_6H_6) with Br in CS_2–$AlCl_3$ (trace) gives *Et₂ αα′-di-(bromoacetyl)-αα′-dimethylsuccinate*, m.p. 55°, which with Ag at 120—150° gives Et_2 3 : 6-diketo-1 : 2-dimethyl*cyclo*hexane-1 : 2-dicarboxylate (**I**) (*di-p-nitrophenylhydrazone*, m.p. 143°). Reduction (Zn–Hg) of (**I**) followed by hydrolysis and steam-distillation affords 1 : 2-dimethyl*cyclo*hexane-1 : 2-dicarboxylic anhydride [deoxycantharidin]. Reduction of (**I**) with $Al(OPr^{\beta})_3$ yields Et_2 3 : 6-dihydroxy-1 : 2-dimethyl*cyclo*hexane-1 : 2-dicarboxylate (*acid*, m.p. 99°), which with conc. H_2SO_4 gives 3 : 6-oxido-1 : 2-dimethyl*cyclo*hexane-1 : 2-dicarboxylic anhydride (separated by sublimation), identical with an authentic specimen of cantharidin. F. R. S.

Pyrrolidines and piperidines.—See B., 1944, II, 306.

Preparation of derivatives of pyrrole and pyridine by hydrogenation. H. A. Adkins, I. A. Wolff, A. Pavlic, and E. Hutchinson (*J. Amer. Chem. Soc.*, 1944, **66**, 1293—1295).—Hydrogenolysis of C–NH_2 occurs readily when β, but not when γ, to the N of pyrrole or C_5H_5N. Pyrrole with MgEtBr and then AcCl in Et_2O gives 2-acetylpyrrole, m.p. 88—89°, the oxime, m.p. 144—145°, of which with H_2–Raney Ni in dioxan or EtOH at 130°/200 atm. gives 2-α-aminoethylpyrrole (56%), which decomposes when distilled and is isolated as *Bz* derivative, m.p. 149—150°. 3-α-Oximinoethylpyridine at 100° gives similarly 3-α-aminoethylpyridine (74%), b.p. 112—113°/12 mm., 223°/740 mm. [*phenylthiocarbamide* derivative, m.p. 139—140°; picrate, m.p. 204—205°; *platinichloride*, m.p. 280° (decomp.)], and *di-(α-3-pyridylethyl)amine* (11%), b.p. 152—153°/1 mm. [*platinichloride*, m.p. 292° and 161—163°; *picrate*, m.p. 205° (decomp.)]. The *oxime*, m.p. 197—198°, of Et 3-acetyl-2 : 4-dimethylpyrrole-5-carboxylate (**I**) (prep. from CH_2Ac_2, OH·N:CAc·CO_2Et, and Zn dust in AcOH) with H_2–Rancy Ni at 130°/200 atm. gives Et 2 : 4-dimethyl-3-α-aminoethylpyrrole-5-carboxylate (80%), isolated as *Bz* derivative, m.p. 179—180°, and converted by distillation into *Et 2 : 4-dimethyl-3-vinylpyrrole-5-carboxylate*, m.p. 110·5—112°, b.p. 145—148°/3 mm. 3 : 5-Diacetyl-2 : 4-dimethylpyrrole gives the *5-mono-oxime*, m.p. 240° (decomp.), hydrogenated at 140—150° to *3-acetyl-2 : 4-dimethyl-5-ethylpyrrole* (30—36%), m.p. 159—160° (? 106—107°). Hydrogenation of (**I**) at 170° gives Et 2 : 4-dimethyl-3-ethylpyrrole-5-carboxylate (95%). That of the *oxime*, m.p. 162—163°, of Et 5-acetyl-2 : 4-dimethylpyrrole-3-carboxylate at 130° gives *Et 2 : 4-dimethyl-5-ethylpyrrole-3-carboxylate* (94%), m.p. 106—107°. That of 3-cyanopyridine at 130° gives 3-pyridylmethylamine (42%), b.p. 112°/18 mm. [picrate, m.p. 210—211° (decomp.); dihydrochloride, m.p. 222°; *p*-nitrobenzoyl derivative, m.p. 188—189°], and *di-3-pyridylmethylamine* (48%), b.p. 147—148°/? mm. (*platinichloride*, m.p. >300°; *picrate*, m.p. 218—220°). Et β-keto-β-3-pyridylpropionate at 80° yields, by hydrogenation and dehydration, unstable Et β-3-pyridylacrylate, b.p. 136—138°/3 mm. (*hydrochloride*, m.p. 186—187°). R. S. C.

Absorption spectra of pyrrole-blue *A* and *B*.—See A., 1944, I, 265.

Chemistry of bivalent and tervalent rhodium. VI. Pyridine complexes of rhodous halides. F. P. Dwyer and R. S. Nyholm (*J. Proc. Roy. Soc. New South Wales*, 1942, **76**, 275—280).—$RhCl_3$ with KBr and C_5H_5N followed by H_3PO_2 at 100° gives *hexakis-pyridine rhodous bromide*, converted by HBr at 0° into the *bromo-pentakis* compound (*iodide*), which with aq. HBr affords *dibromo-tetrakis-pyridine rhodium*. EtOH–HBr with the latter compound yields *dibromo-hexakis-pyridine μ dibromodirhodium*, which on long boiling with EtOH–HBr is converted into a mixture of *bis-pyridinium-tetrabromo-tetrakis-pyridine μ dibromodirhodium* and *tetrakis-pyridinium-hexabromobis-pyridine dibromodirhodium* (both red-brown) and a highly H_2O-sol. compound hexakis-pyridinium-octabromodibromodirhodium. The hexakis compounds are yellow. In the chloride and iodide series certain of the compounds could not be isolated. *Hexakis-* and *chloropentakis-pyridine rhodous chloride*, *bis-pyridinium tetrachlorotetrakis-* and *tetrakis-pyridinium hexachlorobis-pyridine μ dichlorodirhodium*, and *hexakis-* and *iodopentakis-pyridine rhodous iodide* are described. F. R. S.

Co-ordination compounds derived from nicotinylacetone. F. Lions, B. S. Morris, and E. Ritchie (*J. Proc. Roy. Soc. New South* 1942, **76**, 294—303).—Nicotinylacetone (**I**) (*picrate*, m.p. 155°) forms a *methiodide*, m.p. 184°, which with NaOEt gives a *betaine*. $(CH_3·NH_2)_2$ with (**I**) yields *ββ′-ethylenediaminobis(propenyl-3-pyridyl ketone)*, m.p. 170°. The following complexes are described: *Cu nicotinylacetonate*, chars at >320°, *bisnicotinylacetone Cu chloride*, m.p. 190°, and *sulphate* chars at ~280°, *Cu bisnicotinylacetone α-bromocamphor-π-sulphonate* (which could not be resolved), *Zn nicotinylacetonate*, chars at >300°, *bisnicotinylacetone Zn chloride*, m.p. 140°, and *sulphate*, m.p. >300°, *Zn bisnicotinylacetonate α-bromocamphor-π-sulphonate* (non-resolvable), *Ni bisnicotinylacetonate*, chars at >300°, *bisnicotinylacetone Ni chloride*, chars at >300°, and *sulphate*, *Co bisnicotinylacetonate*, *bisnicotinylacetone Co chloride*, *bisnicotinylacetone Ag nitrate*, m.p. 121°, *Fe^{III} nicotinylacetonate*, m.p. >300°, *bisnicotinylacetone Fe^{III} chloride*, m.p. >300° (mol. wt. abnormal), *trisnicotinylacetone Cr^{III} chloride* (+4H_2O), m.p. 105°, *Cu bisnicotinylacetonate methiodide* (+4H_2O), m.p. 188° [*Zn* (+6H_2O), m.p. 146°, and *Be* complexes, m.p. 214°], *Cu ethylenediamine bisnicotinylacetonate* (+H_2O), m.p. 167° (*dihydrochloride*, m.p. 200°), and *Zn*, m.p. 228° (*dihydrochloride*, m.p. 253°), *Ni* (+H_2O), m.p. 258° (*dihydrochloride*, m.p. 276°), and *Co* (+6H_2O) complexes, m.p. 165° [*dihydrochloride*, m.p. 242° (decomp.)]. F. R. S.

Pyridine-3-acetic esters and quaternary compounds.—See B., 1944, II, 306.

Biochemical and bacteriostatic actions of salicylic acid and salicylnicotinylamide. H. von Euler and B. Hogberg [with H. Hasselquist] (*Arkiv Kemi, Min., Geol.*, 1944, **17**, **B**, No. 14, 8 pp.).—*Salicylnicotinylamide*, m.p. 205°, is obtained in 35% yield by the interaction of *o*-OH·C_6H_4·CO·NH_2 and nicotinyl chloride hydrochloride in C_5H_5N at 110° (see A., 1944, III, 844). H. W.

Preparation of pyridine-2 : 5-dicarboxylic acid. T. O. Soine (*J. Amer. Pharm. Assoc.*, 1944, **33**, 223—224).—Quinaldine (20 c.c.) in conc. H_2SO_4 (40 c.c.) is oxidised by cautious addition of HNO_3 (~300 c.c.) with ultimate heating to 230—240°; 7—8 hr. are required. The crude dicarboxylic acid (14·5 g.) is pptd. by addition of 50% NaOH almost to complete neutralisation and cooling to room temp. Decolorising with C and crystallising from H_2O gives the pure acid, m.p. 238° [Me_2 ester, m.p. 161—163°; diamide, m.p. 310—313° (decomp.)]. F. O. H.

Aminosulphanilamidopyridines.—See B., 1944, III, 186.

Catalytic hydrogenation of hydroxy-pyridines and -quinolines and their esters. C. J. Cavallito and T. H. Haskell (*J. Amer. Chem. Soc.*, 1944, **66**, 1166—1171).—Aroyl esters of 2- and 4-hydroxypyridine and -quinoline are more readily hydrolysed than those of the other OH-bases. The 4-acyloxy-compounds must be prepared under anhyd. conditions. The ester linkage of 2-acyloxyquinoline is weakened by 4-Me. Esters described below are prepared from ArCOCl with the OH-compound at 150° or in C_5H_5N at 100° or with the Na derivative thereof in Et_2O. Hydrogenation (Pd; dioxan or, sometimes, EtOH; 55°) of alcohols and esters of these series is reported; its course is various. 2-Hydroxypyridine gives 2-piperidone (**I**), but 3- (**II**) and 4-hydroxypyridine are unaffected. 1-Hydroxy*iso*quinoline gives 1-keto-1 : 2 : 3 : 4-tetrahydro*iso*quinoline (**III**), m.p. 73° (lit. 71°). 3-, 5- (**IV**), 6-, 7-, and 8-Hydroxyquinolines give the corresponding hydroxy-1 : 2 : 3 : 4-tetrahydroquinolines (the 3-*OH*-compound has m.p. 93°), but 2-hydroxyquinoline gives 2-keto-1 : 2 : 3 : 4-tetrahydroquinoline (**V**), and 4-hydroxy- (**VI**), 2-hydroxy-4-methyl- (**VII**), and 4-hydroxy-2-methylquinoline (**VIII**) are unchanged. 2-Benzoyloxypyridine, m.p. 47° (lit. 42°), gives PhMe and (**I**); *3-benzoyloxypyridine*, m.p. 51°, is unchanged; *4-benzoyloxypyridine*, m.p. 79°, gives PhMe and 4-hydroxypyridine. *2-β-Naphthoyloxypyridine*, m.p. 116°, gives 2-$C_{10}H_7$Me and (**I**). 2-p-*Benzyloxybenzoylpyridine*, m.p. 123—125°, gives *p*-cresol and (**I**). 2-3′ : 4′ : 5′-*Tribenzyloxybenzoylpyridine*, m.p. 116°, gives 1 : 3 : 4 : 5-C_6H_2Me(OH)$_3$ and (**I**), but 3-3′ : 4′ : 5′-*tribenzyloxybenzoylpyridine*, m.p. 120°, gives 3-3′ : 4′ : 5′-*trihydroxybenzoylpyridine*, m.p. 180—185°. 2-*Benzoyloxyquinoline*, m.p. 95°, gives PhMe and (**V**); *4-benzoyloxyquinoline*, m.p. 131°, gives PhMe and (**VI**); 3-, m.p. 67°, 5-, m.p. 93°, 6-, m.p. 118° (lit. 230°), and 7-benzoyloxyquinoline, m.p. 85° (lit. 88°), give the derived *benzoyloxy-1 : 2 : 3 : 4-tetrahydroquinolines*, m.p. 106°, 107°, 102°, and 117°, respectively; 8-benzoyloxyquinoline, m.p. 118°, gives *8-hydroxy-1-benzoyl-1 : 2 : 3 : 4-tetrahydroquinoline*, m.p. 174°. *1-Benzoyloxyisoquinoline*, m.p. 187°, gives PhMe, (**III**), and the 2-*Bz* derivative, m.p. 132°, of (**III**). *2-β-Naphthoyloxyquinoline*, m.p. 125°, gives PhMe and (**V**). *2-Benzoyloxy-4-methylquinoline*, m.p. 76°, gives PhMe and (**VII**). 2-3′ : 4′ : 5′-*Tribenzyloxy-*, m.p. 117°, and 2-3′ : 4′ : 5′-*triacetoxy-benzoyloxyquinoline*, m.p. 133°, give (**V**) and 1 : 3 : 4 : 5-C_6H_2Me(OR)$_3$ (R = H and Ac, respectively). *8-p-Benzyloxybenzoyloxyquinoline*, m.p. 163°, gives *8-hydroxy-1-p-hydroxybenzoyl-1 : 2 : 3 : 4-tetrahydroquinoline*, m.p. 161°. *2-Hydroxy-8-benzoyloxyquinoline*, m.p. 208°, gives *2-keto-8-benzoyloxy-1 : 2 : 3 : 4-tetrahydroquinoline*, m.p. 167°, also obtained with PhMe from *2 : 8-dibenzoyloxyquinoline*, m.p. 108°. *1-Benzoyl-8-benzoyloxy-1 : 2 : 3 : 4-tetrahydroquinoline*, m.p. 146°, is also described. (**II**) is obtained from 3-aminopyridine by $NaNO_2$ in conc. H_2SO_4, later warm. NH_2Ph (1) and CO_2Et·CO·CH_2·CO_2Et (1 mol.) at 40—50° and then room temp. give an anil, which in mineral oil at 250° gives Et kynurenate (~60%), whence hydrolysis (4% aq. NaOH; gives the acid, m.p. 280°) and decarboxylation (mineral oil; 270°) gives (**VI**). (**IV**) is obtained from the NH_2-compound by a diazo-reaction. (**VIII**) is obtained by condensing NH_2Ph with CH_2Ac·CO_2Et and heating the product in oil at 250—260°. R. S. C.

Synthesis of oxindole. F. J. Di Carlo (*J. Amer. Chem. Soc.*, 1944, **66**, 1420).—*o*-NO_2·C_6H_4·CH_2·CO·CO_2H (prep. from *o*-C_6H_4Me·NO_2 by $Et_2C_2O_4$–NaOEt in hot EtOH and then hot aq. EtOH), m.p. 119—120°, with H_2O_2 gives *o*-NO_2·C_6H_4·CH_2·CO_2H, hydrogenation of which (AcOH; 50 lb.; PtO_2) gives oxindole (**I**) (88%) or (less PtO_2) 75% of (**I**) and some 1 : 2-dioxindole, *o*-C_6H_4<CH_2>CO>N·OH (**II**), m.p. 198—199° (*brucine* salt, m.p. 223°). (**II**) is unaffected by H_2–PtO_2; thus, the intermediate is *o*-OH·NH·C_6H_4·CH_2·CO_2H, which suffers either ring-closure to (**II**) or further hydrogenation to (**I**).

Dialkylaminoalkyl derivatives of substituted quinolines and quinaldines. A. M. Van Arendonk and H. A. Shonle (*J. Amer. Chem. Soc.*, 1944, **66**, 1284—1285).—4-Chloro-6-methoxyquinoline and the appropriate diamine in boiling *p*-cymene yield 4-*β-diethylaminoethylamino-*, $+H_2O$, m.p. 77—78° (hygroscopic dihydrochloride), 4-*β*-di*iso*butylaminoethylamino- (*dihydrochloride*, m.p. 250—252°), 4-*γ-diethylamino*-n-*propylamino-*, $+2H_2O$, m.p. 165—170°, 4-δ-diethylamino-α-methyl-*n*-butylamino- (dihydrochloride; picrate, m.p. 180—182°), 4-δ-*N*-methyl-*N*-butylamino-α-methyl-*n*-butylamino- (*dihydrochloride*, $+xH_2O$, m.p. 90—91°), 4-δ-*N-iso*propyl-*N-iso*-butylamino-α-methyl-*n*-butylamino- (*dihydrochloride*, m.p. 157—160°), 4-δ-di*iso*butylamino-α-methyl-*n*-butylamino- (*dihydrochloride*, $+xH_2O$, m.p. 104—106°), 4-*γ-piperidino-*, m.p. 134—135°, and 4-*γ*-2′-*pipecolino*-n-*propylamino-*, m.p. 135—137°, -6-*methoxyquinoline*. Boiling 40% HBr then yields 4-*β-diethylaminoethylamino-*, m.p. 245—246°, 4-*β*-di*iso*butylaminoethylamino- (*dihydrochloride*, $+2H_2O$, m.p. 138—140°), 4-δ-diethylamino-α-methyl-*n*-butylamino- (*dihydrochloride*, m.p. 150—153°), and 4-*γ-piperidino*-n-*propylamino-*, m.p. 164—166°, -6-*hydroxyquinoline*. 4-*β-Dicthylaminoethylamino-*, m.p. 145—147°, and 4-*γ*-diethylamino-*n*-propylamino- (dihydrochloride, $+2H_2O$, m.p. 125—126°) -6-methoxy-2-methylquinoline are similarly prepared. R. S. C.

Substituted quinolines. II. 2-Arylquinolines. III. 2-Arylquinolines from fluoranthene and thionaphthen. N. P. Buu-Hoï and P. Cagniant (*Rec. trav. chim.*, 1943, **62**, 713—718, 719—722).—II. Condensation in boiling alcoholic KOH of isatin (I) with the corresponding aryl Me ketone (prep. from hydrocarbon, AcCl, and $AlCl_3$) gives 2-(p-cyclo*hexylphenyl*)-, m.p. 279—280°, 2-α-*naphthyl-*, m.p. 214°, 2-*β*-naphthyl-, m.p. 240°, 2-*β-anthryl-*, m.p. 291—292° (decomp.), 2-(3′-*pyrenyl*-)-, decomp. >300°, and 2-(2′-*chrysenyl*-)-, decomp. >262°, *-cinchonic acid*. These on decarboxylation by fusion in vac. yield 2-(p-cyclo*hexylphenyl*)- (**II**), m.p. 135° (*picrate*, m.p. 162°), 2-α-*naphthyl-*, b.p. 210°/0·1 mm., m.p. 90—91° (*picrate*, m.p. 187°), 2-*β-naphthyl-*, m.p. 164° (*picrate*, m.p. 176—177°), 2-*β-anthryl-*, m.p. 180°, 2-(3′-*pyrenyl*)-, m.p. 145° (*picrate*, m.p. 260° (decomp.), and 2-(2′-*chrysenyl*)-, m.p. 185° (*picrate*, m.p. 225°), *-quinoline*. (**II**) with Se at 350° affords 2-diphenylylquinoline; 2-(5′-*acenaphthyl*)*quinoline*, m.p. 122° (*picrate*, m.p. 231—232°), is described.

III. Fluoranthene with AcCl and $AlCl_3$ in CS_2 gives 12-*acetylfluoranthene* (**III**), b.p. 210°/0·1 mm., m.p. 68° (*semicarbazone*, m.p. 240°; *oxime*, m.p. 166°, giving 12-acetamidofluoranthene by Beckmann transformation). (**III**) with (I) affords 2-(12′-*fluoranthyl*)-*cinchonic acid*, m.p. >310°, decarboxylated to 2-(12′-*fluoranthyl*)-*quinoline*, b.p. 280°/0·1 mm., m.p. 136° (*picrate*, m.p. 242°). 3-Acetylthionaphthen (modified prep.) with (I) gives 2-(3′-*thionaphthenyl*)-*cinchonic acid*, m.p. 229—230° (decomp.), and thence 2-(3′-*thionaphthenyl*)*quinoline*, b.p. 290°/15 mm., m.p. 186° (*picrate*, m.p. 201°). D. G.

Complex compounds of cupric azide. III. Non-electrolytes with organic bases.—See A., 1944, I, 290.

Hydroacridones. Synthesis and dehydrogenation. R. A. Reed (*J.C.S.*, 1944, 425—426).—*cyclo*Hexanone with *o*-$NH_2{\cdot}C_6H_4{\cdot}CO_2H$ (I) gives 1 : 2 : 3 : 4-tetrahydroacridone, m.p. 370° (lit. 358°), whilst with the appropriate methylanthranilic acid, 9-, m.p. 346°, 8-, m.p. 378° (*picrate*, m.p. 208—209°), 7-, m.p. 374°, 6-, m.p. 355° (*picrate*, m.p. 165—185°), and 10-*methyl*-1 : 2 : 3 : 4-*tetrahydroacridone*, m.p. 170—172° (*picrate*, m.p. 209—210°), are obtained. The methyltetrahydroacridones are dehydrogenated with Cu in air at 360° to the corresponding methylacridones. 3-Methyl*cyclo*hexanone with (I) affords 2-methyl-1 : 2 : 3 : 4-tetrahydroacridone [*picrate*, m.p. 212° (decomp.)] (cf. Perkin *et al.*, A., 1925, i, 64), the constitution being proved by dehydrogenation; 2-methyl*cyclo*hexanone with (I) yields the 1-Me compound, m.p. 305° (*picrate*, m.p. 183—184°). F. R. S.

Reaction between histidine and formaldehyde. A. Neuberger (*Biochem. J.*, 1944, **38**, 309—314).—Histidine (I) with 2 or more mols. of CH_2O at 37° gives 1(?1′)-*hydroxymethyl*-1′ : 2′ : 5′ : 6′-*tetrahydropyrido*-4′ : 3′-4 : 5-*glyoxaline*-6′-*carboxylic acid* ($+H_2O$), insol. in H_2O, m.p. 210—215° (decomp.), $[\alpha]_D$ −84·6° in NaOH (1·1N.), which with HCl gives CH_2O and the unmethylolated *acid* ($+2H_2O$), m.p. 277°, $[\alpha]_D$ −122·4° in N-NaOH, also obtained from (I) and 1 mol. of CH_2O, and decarboxylated to 1′ : 2′ : 5′ : 6′-tetrahydropyrido-4′ : 3′-4 : 5-glyoxaline, which with NaOH–BzCl affords 3 : 4-*dibenzamido*-N-*benzoyl*-1 . 2 : 5 : 6-*tetrahydropyridine*, m.p. 215°. The dissociation consts. of the two compounds have been measured and compared with those of (I). The kinetics of the reaction are examined and the CH_2O titration of (I) is discussed. F. R. S.

Glyoxalines.—See B., 1944, III, 217.

Synthesis, some derivatives, and metabolism of αγ-diketo-*n*-octoic acid. A. L. Lehninger (*J. Biol. Chem.*, 1944, **153**, 561—570).—$COMeBu^n$ (I) and $Et_2C_2O_4$ in NaOEt–EtOH at the b.p., followed by H_2SO_4, give the *Et* ester (**II**), b.p. 138—139°/13 mm., of αγ-diketo-octoic acid (**III**), liquid (*Ba* salt). The structure of (**II**) is established by condensation with $NHPh{\cdot}NH_2$ to the Et ester of an acid oxidised to 1-phenylpyrazole-3 : 5-dicarboxylic acid. In 2N-NaOH at the b.p., (**III**) gives (I) and $H_2C_2O_4$. In EtOH with aq. $Cu(OAc)_2$, (**II**) gives a chelated *Cu* derivative, $C_{20}H_{30}O_8Cu$, m.p. 135—137°. With 2 : 4-$(NO_2)_2C_6H_3{\cdot}NH{\cdot}NH_2$ and conc. HCl, (**II**) gives the *Et* ester, m.p. 186—187°, of 1-(2′ : 4′-*dinitrophenyl*)-5(3)-*butylpyrazole*-3(5)-*carboxylic acid*, m.p. 204° (decomp. from 185°), which is similarly obtained from (**III**). With semicarbazide hydrochloride, the Na salt (**IV**) of (**III**) gives 1-*carboxylamido*-5(3)-*butylpyrazole*-3(5)-*carboxylic acid*, decomp. from 80—82° (clear melt at 160—165°), hydrolysed by boiling H_2O to 5-*butylpyrazole*-3-*carboxylic acid*, m.p. 166—167°, also obtained from (**III**) and N_2H_4. Intestinal absorption of aq. (**IV**) by rats is small. (**IV**) does not affect the O_2 uptake of surviving rat tissue slices in PO_4'''–saline buffer, possibly owing to low diffusability, since it causes a slight increase in O_2-uptake by minced or homogenised liver. (**III**) is decarboxylated only very slowly by yeast decarboxylase, and inhibits the yeast decarboxylation of $AcCO_2H$. Hexadecan-*β*-one condenses with $Et_2C_2O_4$ to give a C_{20}-diketo-ester. E. W. W.

Production of riboflavin deficiency with phenazine analogues of riboflavin. D. W. Woolley (*J. Biol. Chem.*, 1944, **154**, 31—37).—4-Amino-5-ribitylamino-*o*-xylene with picryl chloride and NaOAc in aq. EtOH at room temp. gives 2′ : 4′ : 6′-*trinitro*-2-*ribitylamino*-4 : 5-*dimethyldiphenylamine*, which on boiling with NaOAc in EtOH yields 1 : 3-*dinitro*-7 : 8-*dimethyl*-5-*ribityl*-5 : 10-*dihydrophenazine*, m.p. 218—220° (decomp.), reduced (Sn–20% HCl or autoclaving in presence of reduced Fe) to the corresponding $(NH_2)_2$-compound. The diamino- and, to a smaller extent, the dinitro-phenazine derivative produce riboflavin deficiency in bacteria and mice, respectively (cf. A., 1944, III, 752). P. G. M.

***N*-Chlorocarbamic esters.**—See A., 1944, II, 364.

Guanamine derivatives.—See B., 1944, II, 249.

5-Sulphanilamidotetrazole. K. A. Jensen and O. R. Hansen (*Rec. trav. chim.*, 1943, **62**, 658—660; cf. Veldstra and Wiardi, *ibid.*, 627).—The compound, m.p. 170°, obtained from 5-aminotetrazole (I) and *p*-$NHAc{\cdot}C_6H_4{\cdot}SO_2Cl$ (**II**) in C_5H_5N gives AcOH, *p*-$NH_2{\cdot}C_6H_4{\cdot}SO_3H$, $CO(NH_2)_2$, and N_3H with aq. NaOH, and is claimed to be 5-acetylsulphanilamidotetrazole (**III**). The compound, m.p. 202°, from (I) and (**II**) in aq. Na_2CO_3, which with aq. NaOH affords *p*-$NHAc{\cdot}C_6H_4{\cdot}SO_3H$ and (I), is considered to be 1- or 2-acetylsulphanilyl-5-aminotetrazole. (I) with *p*-$NHAc{\cdot}C_6H_4{\cdot}SO_2F$ in C_5H_5N does not yield (**III**). D. G.

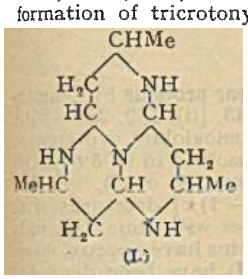
Sulphanilamide derivatives. II. 5-Sulphanilamidotetrazole. H. Veldstra and P. W. Wiardi (*Rec. trav. chim.*, 1943, **62**, 661—671).—In reply to the preceding abstract the authors claim that 5-acetylsulphanilamidotetrazole exists in three tautomeric forms. 5-Aminotetrazole (I) with *p*-$NHAc{\cdot}C_6H_4{\cdot}SO_2Cl$ (**II**) in C_5H_5N gives tetrazoloneacetylsulphanilylimide(-5) (**III**), m.p. 166° (170° on rapid heating), which behaves like a monobasic acid on titration. In aq. Na_2CO_3 (I) and (**II**) yield *β*-5-acetylsulphanilamidotetrazole monohydrate (**IV**), m.p. 202° (on further purification 207°). (**III**) with aq. NaOH affords α-5-acetylsulphanilamidotetrazole monohydrate (**V**), m.p. 207°. (**IV**) and (**V**) show no depression for mixed m.p., and both react as dibasic acids, but are differentiated by electrometric titration curves and ultra-violet absorption spectra. Hydrolysis of (**IV**) and (**V**) (aq. NaOH) gives the same (mixed m.p.) 5-sulphanilamidotetrazole, m.p. 202—203°; (**III**) yields N_3H and $NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH{\cdot}CN$ (?). D. G.

(A) Action of ammonia on crotonaldehyde. (B) Salts and derivatives of tricrotonylidenetetramines. M. Delépine (*Compt. rend.*, 1943, **216**, 649—652, 697—701).—(A) At only slightly >0° $CHMe{:}CH{\cdot}CHO$ (210) and 22% aq. NH_3 (350 g.) give a syrup with only small amounts of crystal, but subsequent keeping at room temp. and then heating at 100° gives tricrotonylidenetetramine-*a*, $C_{12}H_{24}N_4$, $+6H_2O$ (**I**) (50—60 g.), m.p. ~70°, resolidifies, and an *isomeride*-b (**II**) (160—170 g.), (from H_2O) $+6H_2O$ or (from $COMe_2$) $+4H_2O$, m.p. ~65° (instantaneous), b.p. 150°/3 mm. (cf. Wurtz, A., 1879, 780; Combes, A., 1883, 1079). They are separated by crystallisation or by the extreme insolubility of the hydrochloride of (I) in HCl. Over H_2SO_4 in vac., (I) and (**II**) give anhyd. *forms*, m.p. 102°, and an oil, respectively, which are rapidly reconverted into hydrates in air.

(B) (I) and (**II**) give ppts. with Zn, Cd, Hg, Cu, Fe, Co, Al, Cr, Pb, and Sn salts. The following *salts* and *derivatives* prove the tribasicity of the compounds (cf. Kudernatsch, A., 1900, i, 337): (I),$2AgNO_3$,$+3H_2O$; (**II**),$2AgNO_3$,$+2H_2O$; (I) trihydrochloride, insol.; (**II**) dihydrochloride, sol.; 2(I),$3H_2SO_4$,$+12H_2O$ [the sulphate of (**II**) is a glass]; 2(I),$3H_2PtCl_6$,$+12H_2O$, sol.; 2(**II**),$3H_2PtCl_6$,$+12H_2O$, insol.; 2(I),$3H_2IrCl_6$,$+12H_2O$; trireineckates of (I) and (**II**); 4(I),$3H_3Fe(CN)_6$,$+32H_2O$, insol.; 4(**II**),$3H_3Fe(CN)_6$,$+28H_2O$; (**II**),$H_3Fe(CN)_6$,$+4H_2O$; (**II**),$H_3Fe(CN)_6$,$+H_2O$; iridi- and rhodi-cyanides isomorphous with the ferricyanides; tripicrate of (I) [$+4H_2O$; m.p. ~152° (block)] and of (**II**) [$+3H_2O$; m.p. 145—152° (block)]; $(NO)_3$-derivative, m.p. ~240° (block) or (in a tube) deflagrates at ~210°, of (I) [that of (**II**) is amorphous]; N-Cl_3-derivative, m.p. ~76° (tube) or deflagrates

at 70° (instantaneous), of (I) and amorphous, deflagrates at ~40°, of (II). R. S. C.

Constitution of tricrotonylidenetetramines. M. Delepine (*Compt. rend.*, 1943, **216**, 785—789).—A mechanism is proposed for the formation of tricrotonylidenetetramines (I) from CHMe:CH·CHO, whereby the latter (3 mols.) and NH_3 give an aminotriol, $[CHMe:CH·CH(OH)]_3N$, converted by saturation of the double linkings into an intermediate, which then loses H_2O. Oxidation of (I) (α form) (+6H_2O) with aq. $KMnO_4$–KOH at ~0° gives an anhydride (II) (trimeric) of NH_2·CHMe·CH_2·CO_2H (III), sublimes without melting, stable to boiling aq. NaOH–EtOH, and convertible by HCl at 130° for 1·2 hr. into the hydrochloride of (III); Ag_2O, followed by H_2S, then gives (III), m.p. 190°. (I) (β form) does not similarly give (III). (I), heated progressively from 160° to 250—280°, loses NH_3 and ~10% of 2-methyl-5-ethylpyridine is obtained. The α and β forms of (I) probably have the 3 Me groups in different positions. A. T. P.



Synthesis of purine nucleosides. VII. Further observations on the synthesis of pyrimidines from esters and malondiamidine. G. A. Howard, B. Lythgoe, and A. R. Todd (*J.C.S.*, 1944, 476—477).—The pyrimidine synthesis from esters and malondiamidine (I) (cf. Kenner *et al.*, A., 1944, II, 59) has limited val. since no pyrimidine formation occurs with (I) and Et *n*-butyrate, malonate, pyruvate, and urethane, and *N*-acetyl-, phenyl-, and *NN*-dimethyl-urethane. EtOBz and (I) give 4 : 6-*diamino*-2-*phenylpyrimidine*, m.p. 195—196°; Et_2CO_3 gives 4 : 6-diamino-2-hydroxypyrimidine; $ClCO_2Et$ yields 4 : 6-*diamino*-2-*hydroxypyrimidine hydrochloride*, and $Et_2C_2O_4$, 4 : 6-*diaminopyrimidine*-2-*carboxylic acid*, m.p. >360°. NaOAc and Ac_2O convert (I) into 4 : 6-*diacetamido*-2-*methylpyrimidine* (+H_2O), m.p. 232°. F. R. S.

Bile pigments. XXXI. Intermediate products in the conversion of hæmins into bile pigments. E. Stier [with, in part, (Miss) K. Gangl] (*Z. physiol. Chem.*, 1942, **272**, 239—272).—Coproverdohæmin ester is catalytically hydrogenated (Pd in anhyd. HCO_2H at 70—75°) to coproporphyrin I Me_4 ester, identified spectroscopically; the main product is coproglaucobilin ester (I), m.p. 202°. The non-homogeneous course of the oxidation of the copro-ester pyridine-hæmochromogen (II) is shown by the isolation of (I) from the HCl–MeOH mother-liquors of hydroxycopro-ester chlorohæmin by means of Et_2O. Oxidation of (II) with H_2O_2 at 55—60° and then with O_2 followed by treatment with HCl–MeOH gives a very complex mixture of pigments which does not contain (I); a pigment is present which gives a Zn salt which is spectroscopically identical with the Zn salt of dimethoxyætioglaucobilin, but could not be isolated. Similar results are recorded with the meso-ester pyridinehæmochromogen. Successive treatments of the meso-Me_2 ester pyridine-hæmochromogen in C·H_5N with H_2O_2 at 55—60° and BzCl, after removal of Fe by Fe(OAc)$_2$–HCl and treatment with Et_2O, gives *benzoyloxymesoporphyrin* Me_2 *ester* (III), m.p. (indef.) 197—199°, softens at 175°, which is probably a mixture of four isomerides. It is identical spectroscopically with benzoyloxycoproporphyrin. With Zn(OAc)$_2$ in boiling $COMe_2$–MeOH it affords the *complex* $C_{47}H_{44}O_6N_4Zn$, m.p. 232°. Catalytic hydrogenation in AcOH followed by re-oxidation gives only initial material whereas in hot HCO_2H mesoporphyrin and hydroxymesoporphyrin are also produced in small amount. (III) is stable towards HCl–MeOH but readily hydrolysed by NaOMe under N_2; esterification of the product with CH_2N_2 causes complete decomp. but use of HCl–MeOH leads to a hydroxymesoporphyrin Me_2 ester (IV) (not-isolated), spectroscopically identical with hydroxycoproporphyrin ester. The ethereal solution of (IV) is evaporated to dryness and the residue is treated with Fe(OAc)$_2$–NaCl at 100° for 30 sec., thus giving the hydroxymesohæmin Me_2 ester, which could not be obtained cryst.; spectroscopically it is identical with hydroxycoprohæmin ester. It is transformed by air in C·H_5N at room temp. followed by boiling HCl–MeOH into glaucobilin ester which could not be obtained cryst. or as the Zn salt; the yield is very small and a mixture of much red-violet pigments also results. Protohæmin Me_2 ester and N_2H_4 in aq. C·H_5N at 60° give non-cryst. *protohæmochromogen-pyridine-*Me_2*-ester*, from which Fe is removed by dissolution in AcOH–HCl (1 : 1) and which is free from meso- or hæmato-porphyrin. It is converted by the successive actions of H_2O_2 and BzCl in C·H_5N into *benzoyloxyprotoporphyrin* Me_2 *ester*, m.p. 219°, softens at 195°, catalytically hydrogenated (Pd in dioxan) to benzoyloxymesoporphyrin Me_2 ester and hydrolysed by NaOMe in MeOH–dioxan under N_2 at 70° to *hydroxyprotoporphyrin* Me_2 *ester*, which could only be obtained in solution. It is transformed into the amorphous *hydroxyprotohæmin* Me_2 *ester* (yield 25—35%), converted by O_2 in C·H_5N followed by HCl–MeOH into (?) tetramethylhæmatoglaucobilin, which could not be obtained cryst. in very poor yield. Rhodohæmin Me_2 ester and N_2H_4,H_2O in C·H_5N at 80° afford rhodopyridine-hæmochromogen Me_2 ester (+2C·H_5N), m.p. 195°, softens at 182°, transformed by H_2O_2 followed by BzCl into *benzoyloxyrhodoporphyrin* Me_2 *ester*, m.p. 205°, softens at 200°, which resembles chloroporphyrin e_4 and in spectrum. Phyllohæmin Me ester gives successively the *pyridinehæmochromogen* and *benzoyloxyphylloporphyrin Me ester*, m.p. 224° (indef.), softens at 210°, the spectrum of which is displaced somewhat towards the red in comparison with those of phyllo- and dibenzoyloxycopro-porphyrin and identical in type with that of the last substance; it is hydrolysed to *hydroxyphylloporphyrin Me ester*, sol. in Et_2O to a blue solution and giving an ill-defined spectrum. Benzoyloxycoproporphyrin ester is transformed by Fe(OAc)$_2$ and NaCl into the *chlorohæmin*, $C_{47}H_{48}O_{10}N_4ClFe$, m.p. 222°, transformed by N_2H_4,H_2O in C·H_5N at 60° into *α-benzoyloxycopro* I *ester hæm*, m.p. 120—125°. The corresponding pyridine-hæmochromogen is converted by H_2O_2 in C·H_5N followed by Fe(OAc)$_2$ and HCl into *dibenzoyloxycoproporphyrin* I *Me*$_4$ *ester*, m.p. 266°, softens at 200°.

Ætioxanthoporphinogen is transformed by HBr–AcOH at 140—150° into *hydroxyætioporphyrin* I, decomp. 255°. Similarly, meso-xanthoporphinogen is converted into *hydroxymesoporphyrin* IX, m.p. 255—256°, which with HCl–MeOH at room temp. yields the Me_2 ester, m.p. 171°. It is therefore possible to obtain α-hydroxy-porphyrins and bile pigments from xanthoporphinogens and hence the presence of O attached to the α-CH in the xantho-compounds is confirmed. H. W.

Helix pomatia **hæmocyanin.**—See A., 1944, III, 838.

Analgesics derived from oxazolidine-2 : 4-dione. M. A. Spielman (*J. Amer. Chem. Soc.*, 1944, **66**, 1244—1245).—Oxazolidine-2 : 4-dione with Me_2SO_4–aq. NaOH (not *p*-$C_6H_4Me·SO_3Me$) at <40° gives 3-*methyloxazolidine*-2 : 4-*dione*, m.p. 128°. 3 : 5-*Dimethyl-*, b.p. 140—144°/50 mm., 3 : 5 : 5-*trimethyl-* (I), m.p. 46°, b.p. 78—80°/5 mm., 3 : 5-*dimethyl*-5-*ethyl-*, b.p. 101—102°/11 mm., 3-*methyl*-3 : 5-*diethyl-*, b.p. 105—108°/11 mm., 3-*methyl*-3 : 5-*di*-n-*propyl-*, b.p. 100—105°/4 mm., and 5 : 5-*pentamethylene*-3-*methyl-oxazolidine*-2 : 4-*dione*, m.p. 95°, are similarly obtained. Use of EtI and the Ag salt in Et_2O at room temp. (3 days) gives 5 : 5-*dimethyl*-3-*ethyl-oxazolidine*-2 : 4-*dione*, m.p. 61°. These products are analgesic but not hypnotic, notably (I), which is comparable with aspirin and has very low toxicity. 3 : 5 : 5-Trimethylhydantoin (similarly prepared), m.p. 149°, has no pharmacological action, and 3 : 5 : 5-*trimethylthiazolidine*-2 : 4-*dione* (similarly prepared), m.p. 49—51°, is weakly hypnotic. (I) is monoacidic to NaOH (phenolphthalein), yielding this *α-hydroxyisobutyrmethylamide*, m.p. 78—79°. 5 : 5-*Pentamethyleneoxazolidine*-2 : 4-*dione*, m.p. 110—112°, is prepared from Et 1-hydroxy*cyclo*hexanecarboxylate and $NH:C(NH_2)_2$ in EtOH, subsequent hydrolysis being by hot 15% HCl. R. S. C.

Amino-alcohols. 3-Piperidyl derivatives. A. Burger, R. W. Alfriend, and A. J. Deinet (*J. Amer. Chem. Soc.*, 1944, **66**, 1327—1328).—Pyridine-3-carboxyl chloride, b.p. 75—77°/7 mm. (readily hydrolysed in moist air), with CH_2N_2–Et_2O and then 48% HBr gives cryst. 3-bromoacetylpyridine hydrobromide (82%), which with morpholine (3 mols.) in Et_2O yields 3-*morpholinoacetylpyridine* (83%), m.p. 64—68° (*dihydrochloride*, m.p. 197—198°; *dipicrate*, m.p. 158—162°). Al(OPr$^\beta$)$_3$ then yields β-morpholino-α-3-pyridylethyl alcohol (25%) (*dihydrochloride*, m.p. 211°; *dipicrate*, m.p. 166°), hydrogenated (PtO_2; EtOH) to β-morpholino-α-3-piperidylethyl alcohol (45%) (*dihydrochloride*, m.p. 256—257°). R. S. C.

Sulphonamidothiazoles.—See B., 1944, III, 218.

Methine and cyanine colouring matters.—See B., 1944, II, 308, 338.

Fluorocyanine, blue pigment from *Cypridina* **scales.**—See A., 1944, III, 745.

Resynthesis of dethiobiotin from diaminopelargonic acid. D. B. Melville (*J. Amer. Chem. Soc.*, 1944, **66**, 1422).—Passing $COCl_2$ into ζη-diamino-*n*-nonoic acid sulphate (I), micro-m.p. 245—246°, in 10% aq. Na_2CO_3 gives 66% of dethiobiotin (II), micro-m.p. 156—158°, which is fully active in promoting the growth of yeast. (I) is approx. one tenth as active as (II). R. S. C.

Structure-chemical investigations. XI. Reactive behaviour of dithioamides towards tribromotriacetylbenzene. G. Bischoff, O. Weber, and H. Erlenmeyer (*Helv. Chim. Acta*, 1944, **27**, 947—948).—$C_6Ac_3Br_3$ and PhCS·NH_2 in EtOH at 100° afford 1 : 3 : 5-*tri*-(4-*phenyl*-2-*thiazolyl*)*benzene*, m.p. 195°. Complex compounds, becoming discoloured at ~230° or ~250° (decomp.), are obtained from $C_6Ac_3Br_3$ and adip- or oxal-dithioamide. H. W.

Structure-chemical investigations. XII. Thiazole derivatives from terephthaldithioamide. H. Erlenmeyer, W. Büchler, and H. Lehr (*Helv. Chim. Acta*, 1944, **27**, 969—970).—*p*-$C_6H_4(CS·NH_2)_2$ with boiling CH_2AcCl gives 1 : 4-*di*-(4′-*methyl*-2′-*thiazolyl*)*benzene*, m.p. 166° (*picrate*, m.p. 212°), and with COPh·CH_2Br in $PhNO_2$ at 200° affords 1 : 4-*di*-(4′-*phenyl*-2′-*thiazolyl*)*benzene*, m.p. 225°. $(CO·CH_2Br)_2$ in $PhNO_2$ appears to give a complex product, m.p. >360°. H. W.

VII.—ALKALOIDS.

Cleavage of trigonelline. J. Weijlard, M. Tishler, and J. P. Messerly (*J. Amer. Chem. Soc.*, 1944, **66**, 1319—1320).—Trigonelline is unaffected by inorg. sulphides, sulphites, or thiosulphates, BrCN, HNO_2, CrO_3, HNO_3, $HClO_4$, or heating at 290°, but with conc. HCl at 250° (cf. Jahns, A., 1888, 166) or C_5H_5N,HCl at 200—204° gives 83% of nicotinic acid. Use of C_5H_5N,HCl leads also to methylpyridinium chloride. Quinoline hydrochloride is also effective. R. S. C.

Alkaloids of *Duboisia leichhardtii*. W. Mitchell (*J.C.S.*, 1944, 480—482).—*D. leichhardtii* contains *l*-hyoscyamine (1·97%), *l*-hyoscine (0·06%), *dl*-hyoscine (0·05%), norhyoscyamine (0·01%), and "*base D*" (0·06%), isolated as the *hydrobromide* (**I**), $C_{13}H_{23}O_2N$,HBr, m.p. 231° (corr.) (mixture of isomerides). iso-*Valeryltropeine hydrobromide*, m.p. 225—227° (corr.), is not identical with (**I**). Probably at least two distinct types of *Duboisia* have appeared in commerce. F. R. S.

Mode of action of quinine and quinidine. II. Synthesis of 9-hydroxy-6′-methoxyrubans. P. Rabe and W. Schuler (*Ber.*, 1943, **76**, [*B*], 318—321).—(++)(−−)-6′-Methoxyruban-9-ol (**I**) exists as hexahydrate and in *forms*, $+2H_2O$, m.p. 94—95°, and anhyd., m.p. 172°, and gives a very insol. *mono-*, $+6H_2O$, m.p. ~120°, resolidifies, remelts at ~240° (decomp.), and a more sol. *di-hydrochloride*, $+5H_2O$, m.p. ~242°, and *sulphate*, $+4{\cdot}5H_2O$, m.p. 192° (decomp.). The (+−)(−+)-compound (**II**), a glass, gives a *sulphate*, $+6H_2O$, m.p. 86—87° (foams), but its hydrochloride is sol. The isomerides are thus separable. KOH converts (**II**) in boiling C_5H_{11}·OH into (**I**). Reports in the literature are confirmed that (**I**) is active in canary malaria, whereas the (++)- and (−−)-compounds are inactive. R. S. C.

Structure of a new metabolic derivative of quinine. J. Mead and J. B. Koepfli (*J. Biol. Chem.*, 1944, **154**, 507—515).—The cryst. metabolic product (**I**), m.p. 247·5—248·5°, $[\alpha]_D^{25}$ −65·5° in EtOH, derived from quinine (cf. Kelsey *et al.*, A., 1944, III, 680) is probably *l*-2′-hydroxy-6′-methoxy-3-vinylruban-9-ol. Potentiometric titration and absorption spectra for (**I**) and quinine are given. Hydrogenation (H_2–PtO_2) indicates one olefinic linking, and ozonisation affords CH_2O. (**I**) forms a *monomethiodide*, m.p. 276—277° (decomp.), and a *benzenesulphonyl* derivative, $C_{55}H_{68}O_{16}N_4S_3$, m.p. 180—181°, reconverted into (**I**) after mild acid hydrolysis. Attempts at oxidation have afforded no recognisable product. The evidence in favour of the constitution of (**I**) is discussed. M.p. are corr. F. R. S.

[**Alkaloids of**] *Mahonia nepalensis* **DC.** (*Berberis nepalensis*, **Spreng**). R. Chatterjee (*J. Amer. Pharm. Assoc.*, 1944, **33**, 210—212; cf. A., 1944, III, 856).—The root contains 0·48% of umbellatine and 0·02% of *nepratine* (**I**), $C_{19}H_{21}O_3N$, decomp. >200° without melting [*hydrochloride*; *platinichloride* (decomp. without melting)]. Colour reactions for (**I**) with alkaloidal reagents are tabulated. F. O. H.

Synthesis of *l*-roemerine. L. Marion and V. Grassie (*J. Amer. Chem. Soc.*, 1944, **66**, 1290—1292).—*o*-$C_6H_4Me{\cdot}NO_2$, $Et_2C_2O_4$, and NaOEt in EtOH–Et_2O give *o*-$NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CO{\cdot}CO_2Et$, oxidised by H_2O_2–NaOH, later at 50°, to *o*-$NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CO_2H$ (38·6%), m.p. 139—140°. The derived chloride and 3 : 4 : 1-$CH_2O_2{:}C_6H_3{\cdot}[CH_2]_2{\cdot}NH_2$ (modified prep.) give o-*nitrophenylacet-β*-3 : 4-*methylenedioxyphenylethylamide* (74·4%), m.p. 120°, converted by PCl_5 in $CHCl_3$ at room temp. into 6 : 7-*methylenedioxy*-1-o-*nitrobenzyl*-3 : 4-*dihydro*isoquinoline, m.p. 164·5°, the *methiodide*, m.p. 262°, of which with Zn dust in hot aq. HCl gives 6 : 7-*methylenedioxy*-1-o-*nitrobenzyl*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline · *dihydrochloride* (55·4%), m.p. 283—284°. With $NaNO_2$ in 2N-H_2SO_4 at room temp. and then 100° this gives dl-*roemerine* [dl-5 : 6-*methylenedioxyaporphine*] (**I**), m.p. 85—87° (*hydrochloride*, m.p. 274°; picrate, m.p. 197°) (and a *by-product*, $C_{18}H_{19}O_3N$, m.p. 133·5°). The *methiodide*, m.p. 221°, of (**I**) with boiling KOH–MeOH gives the dl-*methine*, m.p. 81° (*methiodide*, m.p. 280°). *d*- and then *l*-tartaric acid yield successively *l*-, *forms*, m.p. 87° and (stable) 102°, $[\alpha]_D$ −79·9° in EtOH [*d*-tartrate, m.p. 264·5° (decomp.); methiodide, m.p. 224·5°], and d-*roemerine*, m.p. 102°, $[\alpha]_D$ +80·2° in EtOH [*l*-tartrate, m.p. 264·5° (decomp.); methiodide, m.p. 224·5°] (cf. A., 1940, II, 197). M.p. are corr. R. S. C.

Isolation of hypaphorine from Argentine species of *Erythrina*.—See A., 1944, III, 856.

VIII.—ORGANO-METALLIC COMPOUNDS.

Arsanilic acids.—See B., 1944, III, 186.

Some new ethyl and phenyl silicon fluorides. H. J. Emeleus and C. J. Wilkins (*J.C.S.*, 1944, 454—456).—*Ethyltri-*, b.p. −4·4°/760 mm., *diethyldi-*, b.p. 60·9°/760 mm., *phenyltri-*, b.p. 101·8°/760 mm., and *diphenyldi-fluorosilane*, b.p. 242·8°/603 mm., are prepared from ZnF_2 and the corresponding chlorides, or from HF and the oxy-compounds. Vals. of *d* and v.p. are given; the latent heats of vaporisation of the first three are 6181, 7623, and 8750 g.-cal. per mol., respectively. The resistance of the compounds to hydrolysis rises rapidly with increase in the no. of org. groups. F. R. S.

IX.—PROTEINS.

Conversion of some spheroproteins into linear proteins by deamination. III. B. Jirgensons (*J. pr. Chem.*, 1943, [ii], **162**, 224—236).—Proteins (**I**) (casein, albumin, edestin, hæmoglobin) are treated with aq. AcOH–$NaNO_2$ and the products dissolved in 0·05N-NaOH (**II**). The η of the solutions is 10—100 times that of (**I**). At low concn. (c), with excess of (**II**), Z_η [$= (\eta - 1)/c$] decreases with increasing c. With excess of (**II**), η decreases with time, but only slowly when c is low. All the degraded proteins have approx. equal Z_η, and behave similarly, suggesting that (**I**) have been degraded into units of approx. equal chain-length. E. W. W.

Viscosity measurements of solutions of deaminated proteins. B. Jirgensons (*J. pr. Chem.*, 1943, [ii], **162**, 237—244).—Serum-albumin and -globulin and gliadin are deaminated and η of solutions in 0·02N-NaOH determined. Z_η of the products are similar to those of other deaminated proteins (see preceding abstract). Z_η of the product of deaminating gelatin (**I**) is $< Z_\eta$ of (**I**), but approx. equals that of the other products, which have much greater aminodicarboxylic acid content. Thus Z_η depends on the unit length of the deamination products rather than on their CO_2H content. E. W. W.

Neglected constituent of proteins, α-amino-*n*-butyric acid. W. C. Tobie (*Nature*, 1943, **152**, 249).—Preliminary work suggests that α-amino-*n*-butyric acid ("quadrine") may occur widely in proteins. Prolonged acid hydrolysis liberates N from the synthetic material, and protein hydrolysis must be enzymic. The name "*iso*quadrine" is suggested for α-amino*iso*butyric acid. E. R. R.

Elucidation of structure of proteins. E. Husemann (*Chem.-Ztg.*, 1943, **67**, 24—28).—A review. W. McC.

Physical and chemical properties of casein from various animal species. E. Kovács (*Biochem. Z.*, 1940, **306**, 74—76; cf. Gróh, A., 1934, 1119).—Examination of caseins from the milk of cow, sheep, goat, horse, and ass shows that the tyrosine, tryptophan, P, and S contents, $[\alpha]_D^0$, and max. and min. absorption of ultra-violet light are subject to species variations of sufficient magnitude to permit identification of unmixed specimens. The magnitude is not sufficient to permit detection or determination of one casein in admixture with another or others or to detect adulteration in curds. W. McC.

Composition of casein in milk.—See A., 1944, III, 818.

Cleavability of keratins treated with hot β-naphthol by proteinases.—See A., 1944, III, 840.

Structure and reactivity of wool keratin. XIII. Keratin fibres shortened by heat.—See A., 1944, III, 818.

Chromosomin, a protein constituent of chromosomes.—See A., 1944, III, 819.

Analysis of a partial hydrolysate of gramicidin by partition chromatography with starch. R. L. M. Synge (*Biochem. J.*, 1944, **38**, 285—294).—Specimens of gramicidin (**I**) from two different sources have been compared in respect of a no. of properties and further information has been obtained about the ultimate hydrolysis products. Preliminary data are provided on the use of raw potato starch as a medium for partition chromatography of free NH_2-acids and peptides. Analysis by this method of a partial hydrolysate of (**I**) has given alanine and *l*-valylglycine, the latter in a yield embodying > half of the glycine of (**I**). The optical form of the valine residues of (**I**) is discussed in the light of new evidence and it is probable that *d*-valine residues will be discovered to be structural components of (**I**). F. R. S.

X.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Phenol groups in lignin. K. Freudenberg and H. Walch (*Ber.*, 1943, **76**, [*B*], 305—308).—Aryl toluenesulphonates are converted by N_2H_4 into *p*-$C_6H_4Me{\cdot}SO_2{\cdot}NH{\cdot}NH_2$ and thence into N_2H_4 *p*-toluenesulphonate, which is determined by addition of the derived acid to $CO(CH{:}CHPh)_2$. This method shows the following contents of phenolic OH in the named varieties of lignin: cuproxam- 1·5, HCl- 1·8, technical HCl-lignin 1·9, lignin of ligninsulphonic acid 2·5, and deacetylated AcOH-lignin 3·0. R. S. C.

Substance, m.p. 260—270° (acetyl derivative, m.p. 192—194°), from black currants.—See A., 1944, III, 783.